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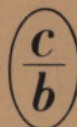
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STUDY OF THE FORMATION MECHANISM OF FERROMANGANESE NODULES AND CRUSTS IN MODERN BASINS.
COMMUNICATION 1. EXPERIMENTS IN SYNTHESIZING Fe, Ni, Cu, AND Co ON MANGANESE HYDROXIDES

I. M. Varentsov, V. S. Putilina,
and L. V. Zaitseva

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Experimental data are presented on the sorptional synthesis of Fe, Mn, Ni, and Co hydroxides on synthetic Mn_3O_4 (hausmannite) and $7 \text{ \AA} MnO_2$ (birnessite). It is shown that the composition of the zones of the newly formed layer is controlled by the initial rates of uptake, a process involving ion-exchange and hydrolysis, and a later process of autocatalytic contact oxidation. The experimental results are interpreted geologically.

Geological research in recent years has convincingly demonstrated that the processes involved in sedimentation-post sedimentation alterations are kinetically controlled and governed only to a very limited extent by the laws of thermodynamics. Microorganisms and organic matter play an especially important role in the sedimentary process. There is increasing evidence tending to support the hypothesis of V.I. Vernadskii that under sedimentary conditions, geochemical processes, including metallogenesis, are controlled to a significant extent by different life forms [7].

Thus, in order to obtain a useful understanding of the geochemistry of the processes of low-temperature sedimentation, or diagenesis (including metallogenesis), the specific and general models for them must adequately reflect the nonequilibrium, irreversible peculiarities of these processes controlled by kinetic and sorption factors.

The Pacific Ocean constitutes an immense metallogenetic system in which three major elements can be distinguished: a) a source of the metals; b) a medium providing for their migration and accumulation; and c) the ore accumulations themselves. The two most extensively developed ore types are nodules (crusts) and metalliferous sediments. The ferromanganese nodules and crusts of many parts of the ocean are regarded today as high-grade ores of Mn, Ni, Co, Cu and other industrially important metals. Despite the existence of sharply differing views regarding the origin of ferromanganese nodules and crusts, the data available have persuaded the majority of researchers that they have been formed by extraction from solutions containing their constituent metals (bottom waters, pore water).

The extraction of microquantities of the transition metals from Mn and Fe hydroxides in seawater (including pore water) is an important problem in the geochemistry of marine metallogenesis. At the same time, the study of the mechanisms whereby trace quantities of the heavy metals are concentrated by Mn and Fe hydroxide collectors or sorbents is a major question in analytical, physical and radiochemistry.

The removal of trace quantities of the transition metals from seawater and pore-water and their accumulation in the form of hydroxides and other phases in ferromanganese nodules and crusts, as well as in sediments, are characteristically very slow processes. Research on the individual steps of metallogenesis in nodules and crusts in the ocean (the matter comprising the nodules and crusts, the composition of the pore solutions and the seawater, the associated sediments, the role of the metal sources, facies conditions, etc.) allows us to make only the most general assessment of the process parameters, and to evaluate only indirectly the chemistry of the phenomenon and the distinctive characteristics of the mechanism.

EXPERIMENTS ON THE SORPTIONAL SYNTHESIS OF Fe, Mn, Ni, AND Co HYDROXIDES
ON MANGANESE HYDROXIDES

Sorptional Synthesis of Fe, Mn, Ni, and Co Hydroxides on Mn_3O_4 . In previous publications [1-3, 7-10] we presented our results on the experimental study of the sorption accumulation

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of a number of heavy metals (Fe, Mn, Ni, Co) on naturally occurring Fe and Mn hydroxides and on synthesized Fe oxides and Mn(FeOOH). This research revealed the basic steps of a complex interaction. It was shown that accumulation occurs over a wide range of concentrations, ranging from ultratrace quantities to quite appreciable contents. With the aid of x-ray diffraction analysis and x-ray photoelectron spectroscopy the composition of the new compounds was identified and the distribution of the valence states of the accumulating metals was assessed. These investigations established that in the multistep reaction being studied, the governing process involved chemisorption (hydrolytic) and the autocatalytic accumulation of the transition metals being studied. The composition of the phases being formed is controlled to a significant degree by the concentration ratios in the solution of the components being accumulated and by kinetic factors.

One goal of the experimental study of the peculiarities of the sorption of Mn, Fe, Ni, and Co from seawater solutions by manganese hydroxides, with hausmannite as an example, was to identify the compositions of the newly formed compounds using different methods, and to assess the relative roles of the factors controlling these processes, and the prospects for extrapolating our results to create models of metallogenesis in recent basins. The major results of these experiments are presented in [2].

In carrying out the experiments on the accumulation of Ni, Co, Mn, and Fe on hausmannite from seawater, great care was taken to keep the conditions the same for all the steps of the interaction. However, the behavior of each of the four constituents being sorbed is characterized by very specific features:

- 1) percentage uptake of Co fell continuously toward the final stages of the process from 40.06 to 15.5%;
- 2) the tendency for uptake to fall off was less marked for Ni than for Co;
- 3) a substantial if gradual increase in percentage uptake is observed for Fe; this rises to as much as 100% in the final steps (after the fifth) of the experiment;
- 4) a gradual decrease in the percentage uptake (from 21.14 to 14.5%) is noted for Mn during the first steps (before the third); in later steps (the fourth to the seventh), a marked desorption of Mn is observed. The amount of Mn that goes into solution in the last steps is appreciably greater than that present in the starting solution. On the basis of an analysis of the adsorption dynamics one can conclude that Mn is not accumulated under the conditions of the experiment, since the amount of Mn that goes into solution in the last stages of the experiment exceeds the amount introduced by 2535 μg . Thus, these data indicate that an amount of Mn equivalent to 16.14% of the sorbed Co or 17.96% of the sorbed Ni was displaced from the structure of the Mn_3O_4 substrate by interaction with Ni and Co in solution.

Study of the surface of the original Mn_3O_4 sorbent and the new products under a scanning electron microscope reveals a number of distinctive features: 1) the original sorbent is characterized by microglobular formations covered by acicular bipyramidal crystals; b) the final product is represented by large globular aggregates with the distinct shapes of the newly sorbed layer, stepped-layer epitaxial overgrowths.

Clearly, flocculation occurred as the sorbed constituents were being accumulated, the particles increased in size, and the needle-like crystallites of the epitaxial overgrowths developed on their surfaces. As a result, the total active surface of the sorbent was substantially reduced during the course of the experiment, which was reflected in the reduced percentage uptake of Co and Ni. Similar relationships were noted in studying the dynamics of the sorption synthesis of oxide phases of Ni, Co, Fe, and Mn on $\gamma\text{-FeOOH}$ type iron hydroxides [1, 9].

The x-ray photoelectron spectra of Co, Ni, and Mn, and the Mossbauer spectra of iron reveal a clear tendency for these elements to be accumulated in relatively high valence states. However, the intensity of oxidation processes at the solution-sorbent interface is relatively lower than for the iron hydroxides ($\gamma\text{-FeOOH}$). A similar distribution of manganese in the experiments with Mn_3O_4 is seen in the comparative enrichment of divalent manganese of the newly formed layer. At the same time, the spectra of the Ni and Co in the newly formed layer retain their resemblance to those of compounds synthesized on lepidocrocite. In this case, however, the distribution of the valence forms of Ni and Co is close to what is observed not in the surface-most part of the layer newly formed on a lepidocrocite substrate, but at a depth of the order of 3400-3500 Å. The overall weakening of the processes of the accumu-

lation of Co, Ni, and Mn on hausmannite compared to lepidocrocite should be noted. The accumulation of the elements does not proceed uniformly: the more active accumulation is observed during the initial stages, and as the new layer develops, the percentage uptake of the sorbed constituents falls off. It is interesting to note that in this case the reduction in the relative proportion of Ni^{3+} and Co^{3+} with depth is more abrupt than in the experiments with lepidocrocite, which is related to the specific influence of the substrate and to the higher rates of accumulation of these metals, as will be shown below.

On the whole, the relationship of the valence forms of Ni, Co, and Mn we observed supports our previous conclusion [1, 9] that the development of the highly oxidized forms of the metals in the outer part of the newly formed layer is related to the reduction in the rates of accumulation of the metals being sorbed. The composition of particular zone of the newly formed layers is clearly controlled by the ratio of the rates of two processes: the initial absorption, a process involving ion exchange and hydrolysis, and a later, autocatalytic contact-oxidation process.

Solid-phase redox reactions occurring as the sorbed ions diffuse into the sorbent structure play a special role. It is precisely these reactions that are responsible for the apparent discrepancy of the data on the absorption dynamics of Mn and the distribution of the valence forms of this metal in the newly formed layer. The results of our experiments, in particular the x-ray photoelectron spectra, provide a better basis for interpreting the displacement of Mn^{2+} and Mn^{3+} from the structure of the manganese hydroxides as Ni and Co are adsorbed. The data suggest that not only is manganese adsorbed and hydroxide phases of this metal formed, but Mn^{2+} is displaced by Ni^{3+} and Co^{2+} , and Mn^{3+} by Co^{2+} in the hausmannite structure, primarily in regions of structural defects. This process is not stoichiometric: an amount of Mn equivalent to 16.14% of the adsorbed Co or 17.96% of the adsorbed Ni goes into solution.

It is important to note that almost all of the iron, the most strongly adsorbed element, is shown by Mossbauer spectroscopy to be present in the newly formed layer in its highest oxidation state, specifically as a compound of the type $FeOOH$.

Sorption Synthesis of Compounds of Fe, Mn, Ni, Co, and Cu on $7 \text{ \AA} MnO_2$ (Birnessite).

These experiments constitute a continuation of the research described above on synthesizing the hydroxide compounds of a number of transition metals (Mn, Fe, Ni, Co) on hausmannite. The experimental conditions were the same in both cases.

It is important to emphasize that in the ore formations of Recent basins the most widely encountered compounds of manganese are $7 \text{ \AA} MnO_2$ (birnessite), $2.4 \text{ \AA}$ (vernadite), and $10 \text{ \AA} MnO_2$. Hausmannite (hydrohausmannite) is encountered more rarely than these other minerals in ferromanganese nodules. Under strongly oxidizing conditions hydrohausmannite is usually a metastable compound that converts to some form of MnO_2 . Because of these peculiarities in the distribution of the phases under investigation in basins, the question inevitably arises as to how specifically the processes of sorption synthesis of the transition metals operate on the two manganese hydroxide minerals Mn_3O_4 and $7 \text{ \AA} MnO_2$.

There are grounds for regarding the sorption reaction as being primarily controlled by the chemistry of the metalliferous solutions: their pH and Eh values, concentrations, the metals present and their speciation, the composition and the abundance of the constituents of the supporting electrolyte, and kinetic factors, which taken all together essentially determine the sign and magnitude of the surface charge of the solid phase, i.e., of the opera-

tional functional groups: $-Mo-OH$; $=Me \begin{matrix} OH \\ OH \end{matrix}$ or $=Me-O-$. On the basis of the fore-

going one can assume that the mechanism of the chemisorption process in the uptake of the transition metals under consideration is essentially the same for both sorbents, hausmannite and birnessite. The differences in the specific surface areas, the details of the distribution of the active sites and functional groups, and the chemistry of the surface be revealed by the kinetics of the process and the details of the interactions between the ions being adsorbed and the structural components of the sorbents.

The experimental data on the uptake of Ni, Co, Cu, and Fe by birnessite from seawater suggest the following conclusions:

1. The uptake of Ni, Co, and Cu does not change appreciably over eight cycles of the experiment. Variations in the percentage uptake are relatively limited: Ni 15.38-50.00%, Co 13.95-45.83%; and Cu 12.19-34.43%.

2. Over the course of the eight cycles of the experiment, the Fe is almost entirely sorbed.

3. For most of the experiment uptake of the transition metals clearly occurred via an ion-exchange process. As a result of these cations being sorbed, appreciable amounts of hydrogen ion were released into the solution, as evidenced by the marked lowering of the pH of the final solution, which fell as low as 0.95 (third cycle). However, along with the protons released by ion exchange, there was also a slight increase in the alkalinity of the final solution for most steps in the second and fifth cycles of the reaction, which points to alkali cations also being displaced during the sorption of the transition metals.

The study of the initial sorbent by transmission and scanning electron microscopy shows that the birnessite used is characterized by a very fine microglobular structure of grain aggregates. Such a highly developed sorbent surface was responsible for the relatively high extraction of Ni, Co, Cu, and Fe during the eight cycles of the experiment. We note that in the runs with γ -FeOOH and Mn_3O_4 described above [1, 2], a reduction was observed in the sorption rates during the final cycles, which was attributed to a substantial reduction in the specific surface area of the sorbent accompanied by the development of stepped microlayers of epitaxial overgrowths of the newly formed layer on the sorbent. Comparison of the initial sorbent (7 Å MnO_2) and the final product under a transmission electron microscope reveals clear evidence of flocculation, aggregation of the sorbent grains, and the development of rims of the newly formed layer along the peripheries of the grains, representing the sorbed layer.

A Mossbauer study of the final product shows that the iron is present as Fe(III). The Mossbauer spectra are almost identical to what was observed for the iron compounds synthesized on Mn_3O_4 . Thus, as a result of Fe being adsorbed by birnessite, a compound of the type FeOOH was formed within the newly formed layer.

The concentration of the other transition metals in the birnessite is relatively low: Ni 0.59%, Co 0.59%, and Cu 0.42%. At such low levels known methods of x-ray diffraction analysis and XPS do not allow the phase composition of the newly formed compounds and the distribution of atomic valence states in the sorbed layer to be determined. In an additional experiment, predetermined amounts of Mn (300-500 µg/liter) were added, in addition to the metals in the experiment discussed above (Ni, Co, Cu, ^{57}Fe). The sorption dynamics of these elements is similar in many ways to what we observed in the other experiments in this series on the powder diffraction diagrams of the final product obtained in the series of individual experiments with 7 Å MnO_2 and taken using a Guinier-de Wolff camera (Fe K_α and Mo K_α radiation; recorded by R. Giovanoli, University of Bern), new lines are distinctly visible that correspond to reflections of a compound such as cryptomelane-hollandite α - MnO_2 .

The experimental data on the synthesis of hydroxide compounds of a number of transition metals on 7 Å MnO_2 are in good agreement with the results of the investigations described in [1, 2, 8, 9]. They are satisfactorily described by the two-step model discussed above, 1) sorption (ion exchange and hydrolytic accumulation) proper; and 2) the interfacial, autocatalytic oxidation of the transition metals sorbed in the first step.

In connection with the above it should be noted that in [4-6] the importance of ion exchange highly selective for heavy metals in the formation of ferromanganese hydroxide nodules and crusts on the sea floor was demonstrated experimentally. The great selectivity of these nodules for heavy metals is regarded as a geochemical barrier of the sorption type, at which the given metals are concentrated from the seawater. It is emphasized that the uptake of heavy, transition metals from seawater occurs via an ion-exchange mechanism, and the excess amounts of Co and Pb in the nodules may be explained by their irreversible sorption without invoking any additional sources of these metals.

GEOCHEMICAL INTERPRETATION

In order to assess the inconsistencies in this genetic model of observations on real nodules it is useful to consider as an example the formation of the Pacific Ocean nodules most enriched in transition metals: those from a region the North Equatorial zone of very high biological productivity and relatively low rates of sedimentation (less than 1 mm/10³ years), and pronounced erosional activity of submarine currents. In the compacted bottom sediments, primarily Upper Tertiary radiolarian oozes, large quantities of fragments of altered basic volcanics are strewn about, palagonites that serve as cores for the majority of the nodules. It is important to note that this nodule field is adjacent to the western slope of the East-Pacific Rise, which is characterized by major hydrothermal activity. The zone

coincides with the tradewind currents. In the upper layers of the water column planktonic organisms extract many transition metals and concentrate them in their flesh and skeletons. Compared to bottom water, porewaters of radiolarian oozes are considerably enriched in certain metals (Mn, Cu, Ni). The bidirectional flow of these metals (upwards from the bottom waters and downwards due to diffusion of the pore solution constituents) is clearly evidenced by the difference in the chemical and occasionally even mineralogical composition of the upper and lower parts of the nodules.

Analysis of the foregoing factors controlling metallogenesis in the nodules in the light of the experimental data presented above allows us to propose the following interpretation [1-3, 7-9]. The metals that accumulated in the nodules (Mn, Ni, Cu, Co, etc.) are present in seawater and pore solutions primarily as the dissolved products of biological (planktonic) processes occurring in the zone of photosynthesis, nodule growth is favored by the presence of fragments of altered basic volcanics, which serve as cores. The presence of Fe and Mn hydroxides in these altered volcanics makes them more active sorbents than the siliceous radiolarian oozes. Low rates of accumulation of the associated sediments favors nodule formation, since the sedimenting particles partly occlude the active sites at which the transition metals are sorbed. A similar function is accomplished by bottom currents, which in addition to removing sedimentary material, also supply fresh batches of metalliferous solution to the zone of natural chromatography. Clearly the favorable action of the bottom currents and the accumulation of biogenic remains enriched in transition metals has been occurring for a geologically long period, since the late Miocene. The concentration of the accumulated components in the bottom water and in the pore solution and the Eh conditions controlled the rates of accumulation and constrained the composition of the ferromanganese hydroxide phases. For example, the following sequence of minerals reflects increasingly oxidizing conditions: $10 \text{ Å MnO}_2 \rightarrow 7 \text{ Å MnO}_2$ (birnessite) $\rightarrow 2.4 \text{ Å MnO}_2$ (vernadite). It is interesting to note that the characteristic sequence of chemisorption and catalyzed accumulation of the transition metal hydroxides is revealed in the microlayers of the epitaxial overgrowths observed with optical and scanning electron microscopes [1, 2, 8, 9]. Comparison of the synthesized hydroxide compounds with naturally occurring nodules shows the presence of many very similar textural features.

LITERATURE CITED

1. I. M. Varentsov, Yu. P. Dikov, and N. V. Bakova, "Towards a model of the formation of Fe ores in Recent basins: experiments on the synthesis of oxide phases of Mn, Fe, Ni, and Co on Mn hydroxides," *Geokhimiya*, No. 8, 1198-1210 (1978).
2. I. M. Varentsov, N. V. Bakova, Yu. P. Dikov, T. S. Gendler, "Toward a model of the formation of Fe ores in Recent basins: experiments on the synthesis of oxide phases of these metals on Mn hydroxides," in: *Lithology at a New Stage of Development of Geological Knowledge* [in Russian], Nauka, Moscow (1981), pp. 270-302.
3. I. M. Varentsov, L. V. Zaitseva, and V. S. Putilina, "Experimental studies on the role of the major ions of seawater in the uptake of Cu(II) by manganese hydroxides: toward the geochemistry of the formation of polymetallic nodular ores in Recent basins," *Geokhimiya*, No. 5, 710-722 (1985).
4. N. F. Chelishchev, "The role of ion exchange in deep-sea mineral formation," *Geokhimiya*, No. 4, 540-547 (1985).
5. N. F. Chelishchev, "Sorption properties of ferromanganese marine nodules," *Geokhimiya*, No. 5, 770-777 (1983).
6. N. F. Chelishchev and N. K. Gribova, "On ion-exchange equilibrium of abyssal marine nodules with seawater," *Geol. Rud. Mestorozhd.*, No. 3, 100-102 (1983).
7. V. S. Putilina and I. M. Varentsov, "Interaction between organic matter and heavy metals in the waters of Recent basins: a review of the current state of the problem," *Chem. Erde*, 39, 298-310 (1980).
8. I. M. Varentsov and N. V. Pronina, "On the study of mechanisms of iron-manganese metallogenesis in Recent basins: the experimental data on nickel and cobalt," *Miner. Deposita*, 8, No. 2, 161-178 (1973).
9. I. M. Varentsov, Yu. P. Dikov, and N. V. Bakova, "On the study of Fe-Mn Metallogenesis in Recent basins: experiments on the synthesis of Mn, Fe, Ni, Co hydroxide phases on iron hydroxides (γ -FeOOH)," *Geol. Geochem. Manganese*, Pub. House Hungarian Acad. Sci., (1980), Vol. 3, pp. 91-104.
10. I. M. Varentsov, L. V. Zaitseva, and V. S. Putilina, "On the geochemistry of nodular polymetallic ore formation in Recent basins: experimental data on the role of major ions of sea-water in the process of copper sorption by manganese hydroxides," *Chem. Erde*, 44, 193-225 (1985).

MINERALOGY AND FORMATION PROCESSES OF OXIDIZED Fe AND Mn SUBSTANCES
IN THE RED SEA RIFT ZONE.

PART I. ORE MINERALOGY

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Based on a complex of physical and chemical methods, the authors have identified the basic structural and crystallochemical characteristics and distribution patterns of Fe- and Mn-oxide and hydroxide compounds that are widespread in the ore matter of hydrothermal-sedimentary deposits of the Atlantis-II and Tethys Basins in the Red Sea.

The solution of a number of problems, related to the formation conditions and mechanisms of hydrothermal-sedimentary deposits in active zones of the world ocean is only possible through detailed studies of their mineral composition.

As known, Fe- and Mn-oxides and hydroxides represent the basic components of the ore matter in metal-bearing sediments. Their mineral composition, structural and crystallochemical characteristics, paragenetic associations and mutual transitions depend greatly on changes in the physicochemical conditions of the medium and therefore should be regarded as important genetic indicators of the surrounding natural conditions. In other words, the presence of given iron- and Mn-oxide and hydroxide minerals in hydrothermal-sedimentary deposits, their compositional and structural characteristics provide valuable information on the routes and physicochemical formation conditions of these sediments.

The rift zone of the Red Sea provides a most interesting subject area for the study of hydrothermal-sedimentary mineralization; the geological and physicochemical formation conditions of these deposits are fairly well known [1, 4, 9, 10, etc.].

The metal-bearing Red Sea sediments occur in the central trough of the rift zone, and are usually found in geomorphologically clearly marked basins. We have selected two of these (the Atlantis-II and Tethys Basins) for the study of mineral phases in the ore matter.

The selection was based on the fact that these basins differ significantly in morphology, in the physicochemical conditions of sedimentary ore matter and in its composition. They are characterized by high ore content of the enclosing sediments and had been well studied in terms of the lithological-geochemical background and characteristics of the ore-forming processes.

It should be noted that despite the great interest in the Red Sea sediments and the relatively high level of related studies, one encounters detailed description of the mineral matter in the ores in only a handful of publications. Most of these deal with the Atlantis-II Basin deposits.

One of the first papers on the subject was published by Bischoff. He subdivided the metal-bearing sediments of the Atlantis II Deep into the following "phases," on the basis of the dominant minerals: 1) detrital; 2) Fe-montmorillonite; 3) goethite and amorphous Fe-hydroxides; 4) Mn-sideritic; 5) anhydritic; 6) sulfide and 7) Mn-phases [1]. In addition to the most abundant amorphous hydroxides, he found lepidocrocite and goethite in the iron oxide phases. Hacket and Bischoff [11] found widespread occurrence of hematite in the Atlantis-II Deep and in one of the cores hematite associated with well crystallized magnetite. In addition to manganite, the Mn-phases locally also included todorokite and groutite. The most typical facies indicator mineral was woodruffite [1]. The formation conditions of Mn-bearing layers in the sediments of the Atlantis-II Deep were "totally incomprehensible," according to

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Bischoff [1, p. 188]. He assumed that the Mn-hydroxides formed locally through weathering of Mn-siderite layers. However, he did not supply any evidence for this. It has been shown [11] that layers, greatly enriched in Mn, are composed mostly of manganite, characterized by a wide range of particle sizes and uneven degrees of crystallization. The Mn-ore deposits in the Atlantis-II Deep, following Bischoff were designated manganese facies of horizons in the literature. As will be shown in the following, this does not express satisfactorily the complexity of their mineral content.

The mineralogy of the sediments in the Tethys Deep has been less well studied. Only one publication [10] provided a full description of the sediment beds and the enclosed minerals, but without any interpretation of their characteristics and genetic conditions. Among the iron oxide phases the authors [10] noted the widespread presence of magnetite, "limonitic" matter and minor amounts of lepidocrocite and hematite. Manganese compounds were characterized as Mn-facies, represented by finely dispersed, poorly crystallized Mn-matter. No diagnostic methods and specific mineral descriptions were included in that work.

Analysis of data in the literature generally indicated that both the mineralogical characteristics of Mn- and Fe-oxide and hydroxides phases in the metal-bearing Red-Sea sediments and the interpretation of their genetic processes have been treated in a generalized manner. No specific conditions were suggested for the formation of Mn-hydroxides. This is understandable, due to the problems involved. On one hand, the high dispersion rate, the low degree of structural ordering in the minerals, and the many components in the samples greatly encumber not only the recognition of fine crystallochemical entities in the studied phases but also their reliable identification. The use of traditional methods for the study of such objects is not effective. On the other hand, until the present time those thermodynamic and kinetic factors that controlled the formation of a given mineral or mineral associations in stable and metastable conditions were only poorly known.

The generally insufficient character of mineral studies on metal-bearing sediments is reflected by the limited nature of data that deal with the correlation of morphological, structural and crystallochemical mineral characteristics with specific conditions of sedimentation. Thus the required data base has been missing for recognizing the mineral-forming mechanisms.

One of the present authors has earlier produced data on the mineral composition of ore matter in the Atlantis-II Deep that led to recognition of mineral parageneses, allowed the tracing of their alterations in the section and in a given area and the characterization of the morphology and structure of ore formations, accompanied by descriptions of x-ray and electron microscope study results [2]. The general genetic concept of the genesis of the main mineral phases was based on these studies in the Atlantis-II Deep [3]. However, even this work included x-ray diffraction analysis as the main diagnostic method. This method, as noted, does not reveal details of mineral structures, their interaction during transformation that are needed in a number of instances, especially in Mn-oxide compounds.

The present paper consists of two parts. Detailed study results of Fe- and Mn-oxide and hydroxide phases in Red Sea ore-bearing deposits (based on the Atlantis-II and Tethys Basin data) were acquired through a complex of up-to-date physical methods. In addition to traditional x-ray diffraction and microprobe analyses, scanning and transmission microscopes were also used, employing electron microdiffraction and localized energy-dispersive chemical analyses of individual microparticles. The authors aimed at a complete description of the mineral composition of the Fe- and Mn-compounds and the establishment of possible genetic connections between various minerals and the lithological-geochemical conditions of their locations. This would lead to the understanding of the various directions and mechanisms of their genesis.

Part I describes the mineral phases of the ore matter; Part II will attempt to interpret the basic formation processes.

THE ATLANTIS-II DEEP

The deposits of this basin are characterized by the great variety and variability of the chemical and mineralogical composition between different parts of the basin and within the cross sections of the ore beds. Bäckér and Richter subdivided the sediment units of the basins on the basis of the dominant mineral components. The following lithofacies zones were established (from bottom-to-top): detrital-pyrite-bearing (DP), lower sulfide zone (SU1), central oxidized zone (CO), upper sulfide zone (SU2), and the amorphous zone (AM) [9].

TABLE 1. Distribution of Iron Minerals in the Sediment Sequence of Atlantis-II Deep

Section 1905 (4)					Section 1905 (5)				
horizon, cm	goethite	hematite	lepidocrocite	ferrhydrite	horizon, cm	goethite	hematite	lepidocrocite	ferrhydrite
5-10	Traces	+	—	×	0-5	—	+	—	×
70-77	+	×	—	—	100-110	Traces	+	—	—
252-257	+	×	—	×	255-265	»	+	—	—
290-300	+	Traces	—	—	350-374	—	+	—	—
338-350	—	—	+	×	483-500	—	—	+	×
355-358	+	×	—	—	500-510	+	×	—	—
367-377	+	×	—	—	520-525	Traces	+	—	—
470-480	×	+	—	—					
555-557	×	+	—	—					

Note: Mn-ore layers shown in thick type; +) dominant mineral, x) secondary mineral; dash) absence of mineral.

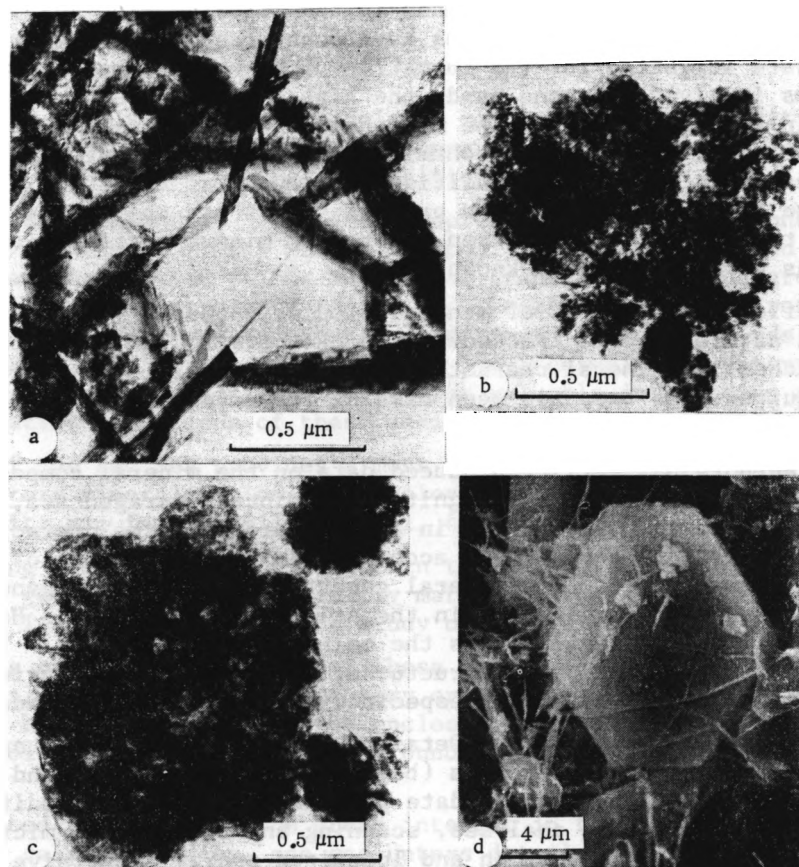


Fig. 1. Morphological hematite and goethite features in sediments of the Atlantis-II Deep: a) goethite crystal laths, station 1905(4), 290-300-cm horizon; b) finely dispersed goethite particle-aggregate, station 1905(4), 252-257-cm horizon; c) aggregate of fine lamellar hematite, station 1905(5), 520-525-cm horizon; d) single hematite crystal from sediments of the SW part of the basin.

Based on its volume, iron was the predominant ore element in all zones; sharply outlined Mn-layers developed locally and were confined to the central oxidized zone (CO).

The study of the mineral composition of iron and manganese oxide compounds was confined to two type sections: a 575-cm thick bed at station 1905(4), 21°22.8'N, 38°05.3'E, and a 580-cm thick bed at station 1905(5), 21°20.5'N, 38°06.1'.

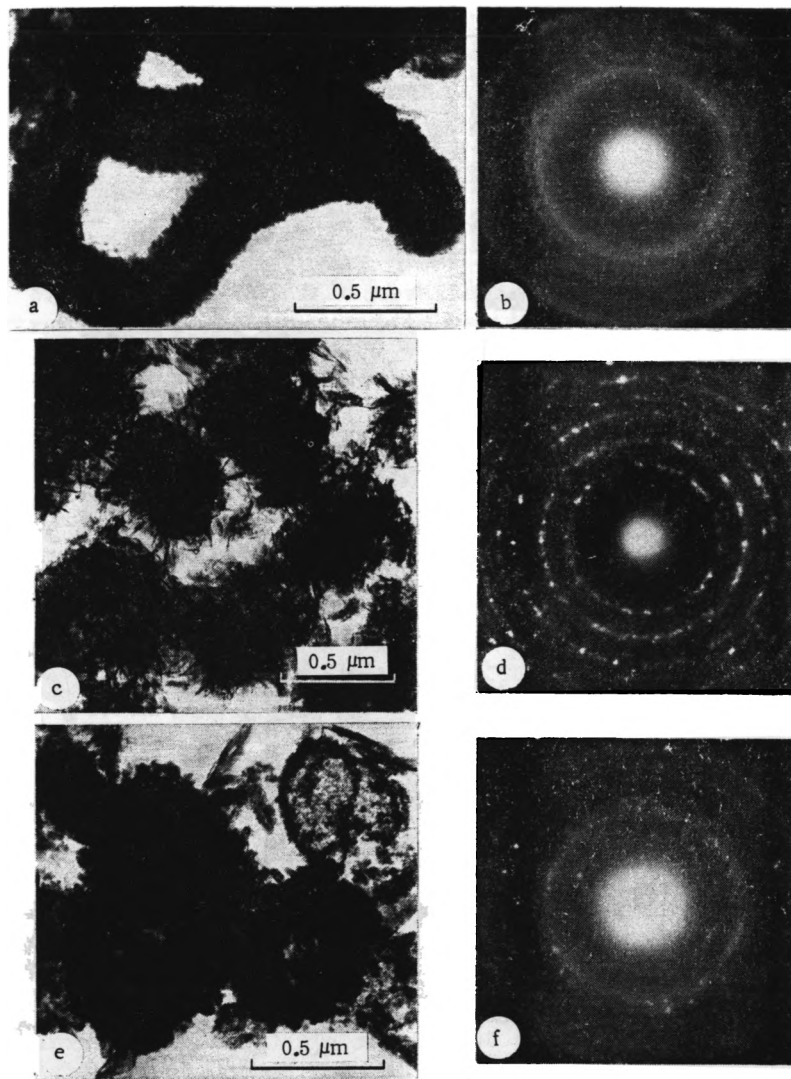


Fig. 2. Electron-microscope images and microdiffraction patterns of ferrihydrite and lepidocrocite particles (Atlantis II Deep). a) ferrihydrite particle aggregate of bacterial origin, station 1905(5); 5-10-cm horizon; b) annular electron-diffraction pattern of ferrihydrite particles, station 1905(5), 483-500-cm horizon; c) globular aggregates of needlelike lepidocrocite particles, station 1905(5), 483-500-cm horizon; d) annular electron pattern of lepidocrocite particles; e) aggregates of lepidocrocite particles of bacterial origin, station 1905(4), 338-350-cm horizon; f) annular electron-diffraction pattern of bacterial lepidocrocite particles, station 1905(4); 338-350-cm horizon.

Iron Oxide and Hydroxide Forms. 17 samples, representing all lithofacies, with the exception of the lower DP zone, from which on core was available, were subjected to detailed mineral analysis.

Table 1 shows the distribution of iron minerals in the studied sections. Iron represented 30-40%, Mn 0.1-2.7%. Mn(IV) was totally absent, while the Mn^{2+} cations occurred in Mn-siderites, unevenly distributed throughout the entire sediment body.

Layers and lenses of sediments that were most enriched in iron usually have reddish-yellow, rose-red and waxy-red hues, depending on the basic mineral composition and the amount of biogenic-terrigenous admixtures. The E_{pt} values ranged between +170-+250 mV.

In general, the iron phases are slightly crystallized, although there is a clear tendency toward a greater structural ordering with increasing burial depth.

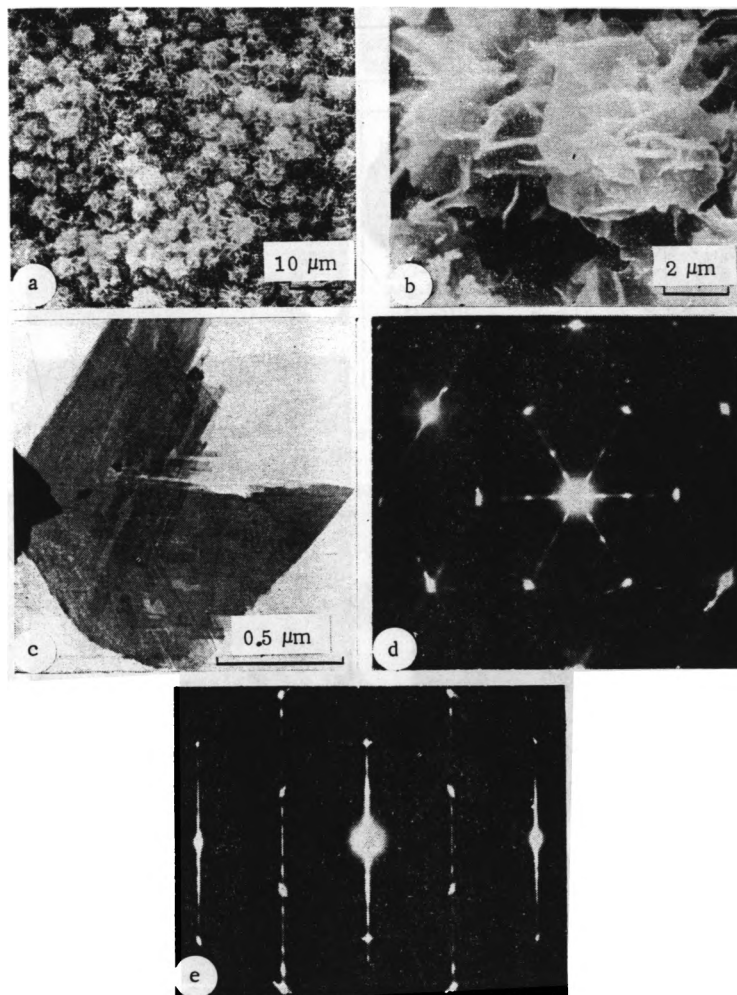


Fig. 3. Electron-microscope images and electron dot patterns of todorokite particles that form the main mass of Mn-ore horizons in the Atlantis-II Deep. Station 1905(5), 483-500-cm horizon. a, b) globular todorokite particles (a - 1500 $\times$ magnification; b - 7500 $\times$ magnification); c - twinned todorokite growth; d-e - electron dot pattern (d - from triple-twinned todorokite growth, $a = 9.75 \text{ \AA}$; e - from todorokite micromonocrystal, $a = 24.4 \text{ \AA}$).

The use of the electron-microdiffraction method, in combination with the x-ray-diffraction method offers a needed diagnostic tool for the entire Mn and iron-oxide mineral complex in the investigated samples. Two minerals, goethite $\alpha\text{-FeOOH}$ and hematite, Fe_2O_3 occurred in all samples of the iron ore deposits.

As a rule, one of these minerals predominated in a given sample and the distribution of the two minerals showed an irregular distribution pattern within the ore body (Table 1).

Goethite occurred in two different forms: as flat, lathlike microcrystals, elongated parallel with the c axis (Fig. 1a), or as aggregates of finely dispersed particles of 30-50 $\text{\AA}$ diameter (Fig. 1b).

Hematite also occurred in two forms. Figure 1c shows electron-microscopic images of a dense aggregate of fine lamellar hematite particles with lathlike goethite crystals. Well-crystallized hematite, in combination with goethite, has earlier been noted in sediments in the southwestern Atlantis-II Deep, in the immediate vicinity of underwater springs [2]. The hematite particles had the typical hexahedral form; the crystals were 0.02-0.04 mm long, and 2-4 μm thick (Fig. 1d). Sediments that had been enriched in this hematite form occur as lenticular bodies in mud bodies. Sharply isolated layers occur at the hydrothermal vents.

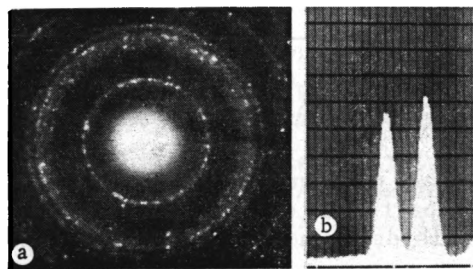


Fig. 4. Electron diagram pattern (a) and electron dispersion spectrum (b) of goethite-groutite particles from the Mn-ore horizon ground mass, Atlantis-II Deep, Station 1905(5), 483-500-cm horizon.

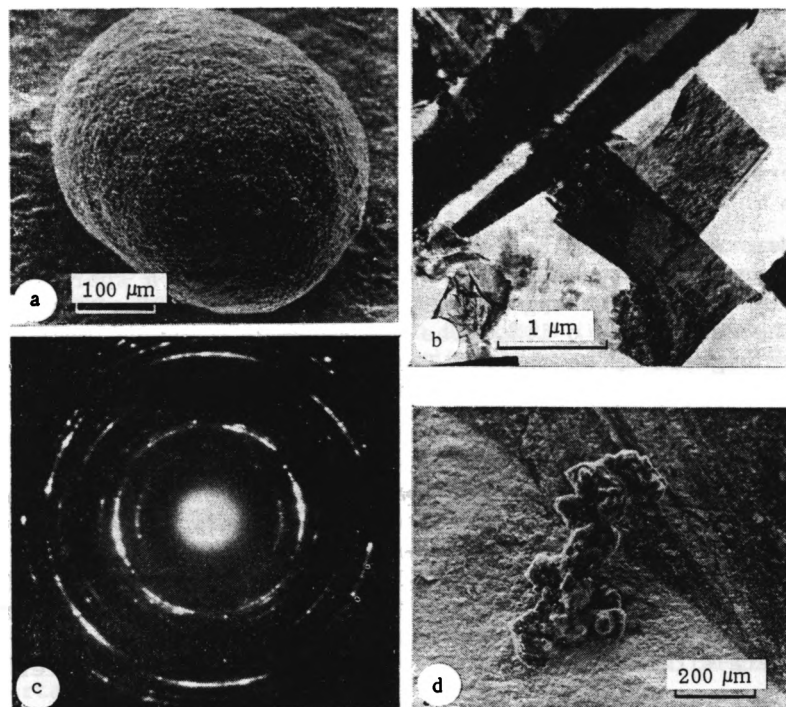


Fig. 5. Morphological features of concretions, developed in the ore groundmass, with manganite diffraction patterns. Station 1905(5), 483-500-cm interval; a) manganite microconcretion; b) lamellar manganite crystals; c) electron diffraction pattern of manganite crystals; d) multicomponent-concretion, including tdo-rokite, manganite and goethite-groutite.

Ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) deposits in the investigated sediments were most interesting from the genetic and mineralogical point of view. The identification of this peculiar mineral was only possible through the electron-microdiffraction method.

The electron-microscope studies indicated that ferrihydrite occurred in bacterial-like aggregates of very fine (30-50 Å) particles (Fig. 2a). The analysis of these images suggests the important role iron bacteria *Gallionella ferruginea* and *Leptothrix ochrocea* [5] played in ferrihydrite formation. The annular electron-diffraction pattern, typical of these minerals is shown in Fig. 2b. The mineral in core 1905(5) occurred only in the surface horizon (0-5 cm) and in core 1905(4) trace quantities of ferrihydrite occurred in the upper, maximum 2.5-m-thick sediment layer (Table 1).

The goethite-ferrihydrite association, typical of the iron-rich sediments, changes to another association in the Mn-ore layers. It contains a mixture of $\gamma\text{-FeOOH}$ lepidocrocite and ferrihydrite.

Two basic particle form types categorize also lepidocrocite and reflect different formation mechanisms. In certain samples the lepidocrocite particles are elongated, needlelike crystals, a fraction of one micron in size. Apparently, they formed in a matrix of gellike spheroidal substance (Fig. 2c). In other samples, the mineral particles clearly are of bacterial origin (Fig. 2e).

Comparison of electron-diffraction patterns of morphologically diverse lepidocrocite particles (Fig. 2d, f) indicated that particles of bacterial origin have a lower level of structural ordering and also include ferrihydrite admixtures.

According to data in the literature, magnetite locally forms near hydrothermal vents [11]. We have not found this mineral in our samples.

Forms of Mn-Oxides and Hydroxides. Ore deposits that consisted of Mn-oxide minerals were atypical of the Atlantis-II Deep. As noted, Mn occurs mostly in Fe-Mn carbonates (Mn-siderites), widespread throughout the sediment beds and responsible for the 2-2.7% Mn content in the sediments (in contrast with the 0.41% background value). Mn(IV) was totally absent from the compounds. The Mn-ore horizons of oxides and hydroxides occur locally and have a strictly defined distribution pattern areally and within the section. In the section these occur in the central oxide zone (CO), between two sulfide zones. Areally they occur near elevated zones of the seafloor, near the basin rim and also outside the brine zones.

Two ore horizons were studied in detail: core 1905(5), 335-350-cm interval; and core 1905(4), the 483-500-cm interval.

Visually, these layers are sharply outlined in the section, by their uniform, dark, almost black color, with cherry-brown hues, a typical "oily" consistency, a sharp boundary toward the enclosing muds. The layers, according to our data and [1, 2] were 15-40 cm thick, their Mn-content was 30-45%, the Fe content 6-11%. The sediments were characterized by redox potential values that were the highest among the Red Sea ore muds ($E_{Pt} = +500$ - $+600$ mV).

Mud samples from two cores showed practically identical mineral composition, not only visually and microscopically, but also according to structure, mineral composition, and geochemical characteristics. Sediment studies by polarizing and scanning electron-microscope studies showed that they consist of a finely dispersed microglobular groundmass that includes numerous dense, individual components of 0.2-0.5 mm size, rarely reaching 1 mm. These represent hard, nodular microconcretions and concretions and crusts of various odd shapes. As the diffraction- and electron-microscope studies have shown, individual Mn-ore categories (groundmass, nodules and various concretions) differ not only in the textural-morphological characteristics, but also in the mineralogical composition. The degree of crystallization differs between the different minerals and there are also certain geochemical differences.

The groundmass of ore matter (type I) is composed of 2-6- μ m globules, made up of rosetta-like lepispheres. Their margin is composed of 2-4 μ m wide typical crystals (Figs. 3a, b). Greatly enlarged electron-microscope images revealed that the crystals have lamellar shapes and occasionally form growths, similar to twins and triple twins (Fig. 3c). Mineralogically, the groundmass consists mostly of todorokite. Its presence is proven by diffraction pattern reflection values ($d = 9.58, 4.78, 2.40, \text{ and } 2.20 \text{ \AA}$). However, one should also note that these reflections are also very typical of four Mn-hydroxide varieties that structurally differ greatly from todorokite. For this reason, the required todorokite identification and the todorokite predominance in the groundmass of Mn-ore layers was established by a combination of x-ray and microdiffraction methods. The analysis of the electron diffraction pattern of the investigated samples indicated that three todorokite varieties exist in the Mn-rich horizons of the Atlantis-II Deep with a -values of 9.75 (Fig. 3d), 19.5 and 24.4 $\text{\AA}$ (Fig. 3e), associated with uneven canal dimensions in the tunnel-like microcrystal structure of the mineral. The crystallochemical characteristics of the various todorokite varieties are explainable by the fact that the ratio values between various Mn cations of different valences increase with increasing tunnel dimensions in the crystal structure [7].

The groundmass contains mostly a todorokite variety with an a -value of 9.75 $\text{\AA}$. Sometimes, the same particle contains structural varieties with different a -values.

The ore groundmass is crystallochemically and genetically quite interesting when it consists of short columnar microcrystals of 0.1-0.15 μ m size. Their electron-diffraction patterns (Fig. 4a) corresponds to diffraction patterns of the goethite, α -FeOOH and groutite, α -MnOOH, that have the same structure. In agreement with data of local energy dispersion an-

alysis, obtained from different portions of the minerals, Mn and Fe occur in similar quantities (Fig. 4b). The data indicate either that an isomorphic replacement of $Mn^{3+} \rightleftharpoons Fe^{3+}$ occurs in the structure of the studied substances or that goethite and groutite develop on a submicroscopic scale. For this reason, this phase may be named the goethite-groutite phase.

In addition to todorokite and goethite-groutite, individual samples of the ore groundmass also contained traces of buzerite-II, a layered 10 Å Mn-oxide. The octahedral Mn^{4+} -layers consist of vacant octahedra. Mn^{3+} , Mn^{2+} , Ca, and other cations, below and above the octahedra are coordinated with water molecules [6].

The study of ten samples by microsonde "Kamebaks" revealed significant chemical variations in the finely dispersed groundmass. While Mn-oxides predominated (55-93% in different locations), Fe-admixtures displayed uneven concentrations (0.14-11.6%), as did Si (0.3-6%), Ca (0.3-1.7%), Mg (1-1.6%). Trace elements included the most abundant Zn (0.02-1.5%) and Pb (0.05-0.5%).

The presence of Si, Mg, Ca, and partially Fe in the ore groundmass apparently is related to the unevenly distributed minor amounts of admixed normal sediment matter and authigenic smectites, as well as cations in the Mn-hydroxide adsorbed complex. Important iron admixtures exist in goethite-groutite, lepidocrocite and ferrihydrite.

The second ore category of the Mn-horizons is represented by black, dense, nodular microconcretions with shiny surfaces. Morphologically these are quite varied; spherical, oval, dumbbell-shaped, often with oblate growths on the basal surface (Fig. 5a). The interior of the microconcretions contains unoriented microcrystals (2-5 µm) of elongated lamellar forms (Fig. 5b). These ore are typically monomineralic in composition. The microconcretions contain well crystallized manganite, as shown by the diffraction patterns and electron microdiffraction data (Fig. 5c). Localized energy dispersion analysis indicated the absence of any other cation in the manganite particles, but Mn. According to microprobe studies, different spots within the microconcretions contain very minor amounts of Fe (0.05-0.5%) and Mo (0.08-0.1%).

Finally, the third morphological variety within the Mn-ore horizons is represented by fine crust particles (the size of a fraction of a mm) and also by concretions of irregular, odd, very varied outlines. They often have branching, dendritic, angular shapes (Fig. 5d). These concretions are relatively brittle, lusterless, heterogeneous, of dark gray color, scoriaceous, with rough, nodular surfaces. They are of mixed mineral and chemical composition, transitional between the first two categories. Todorokite occurs as twinned and tripled-twinned growths according to the electron microscope images. Micromonocrystals are rare. All three of the mentioned todorokite categories occur in these types of samples. However, the $a = 19.5$ Å variety is the most common. Minor amounts of goethite-groutite admixtures have been identified in certain samples.

The Mn-oxide content is generally higher in these materials than in the groundmass, but lower than in the reniform microconcretions (94-96%). The ratios of the accompanying chemical elements are identical to that of the groundmass but their concentrations usually are lower.

TETHYS DEEP

Deposits of this basin generally contain large ore concentrations and their metal content is comparable with those of the Atlantis-II basin sediments. Earlier studies of a 510-cm sediment sequence (station 224; 22°47.2' N; 37°35.5' E) established the general composition of the ore body and the mineralogical-geochemical characteristics [4]. Five distinct, rhythmically alternating members occur in the studied sequence (Fig. 6).

Horizons II and IV have uneven, variegated coloration, dominantly of orange, yellow, and greenish hues. Sooty-black layers and bright, waxy red lenses appear against this background. They are composed almost entirely of iron ore matter of a complex mineralogy. A significant part of the total iron, 32-56% of the samples, consists of mobile, reactive Fe(II) and Fe(III) forms. The Mn- content represents background values that are typical of the common Red Sea sediments (0.35-0.47%). Biogenic-terrigenous sediments are almost nonexistent ($CaCO_3 < 1\%$). The sediments contains increased amounts of copper.

Deposits of Units I, III, and V have more uniform color and consistency. These usually are dark brown, indistinctly banded muds, with rare light-gray layers, composed of two genetically different components: normal sedimentary, dominantly biogenic matter, with high $CaCO_3$ concentrations (20-40%), and ore matter, with both Fe and Mn, present in similar amounts (Mn =

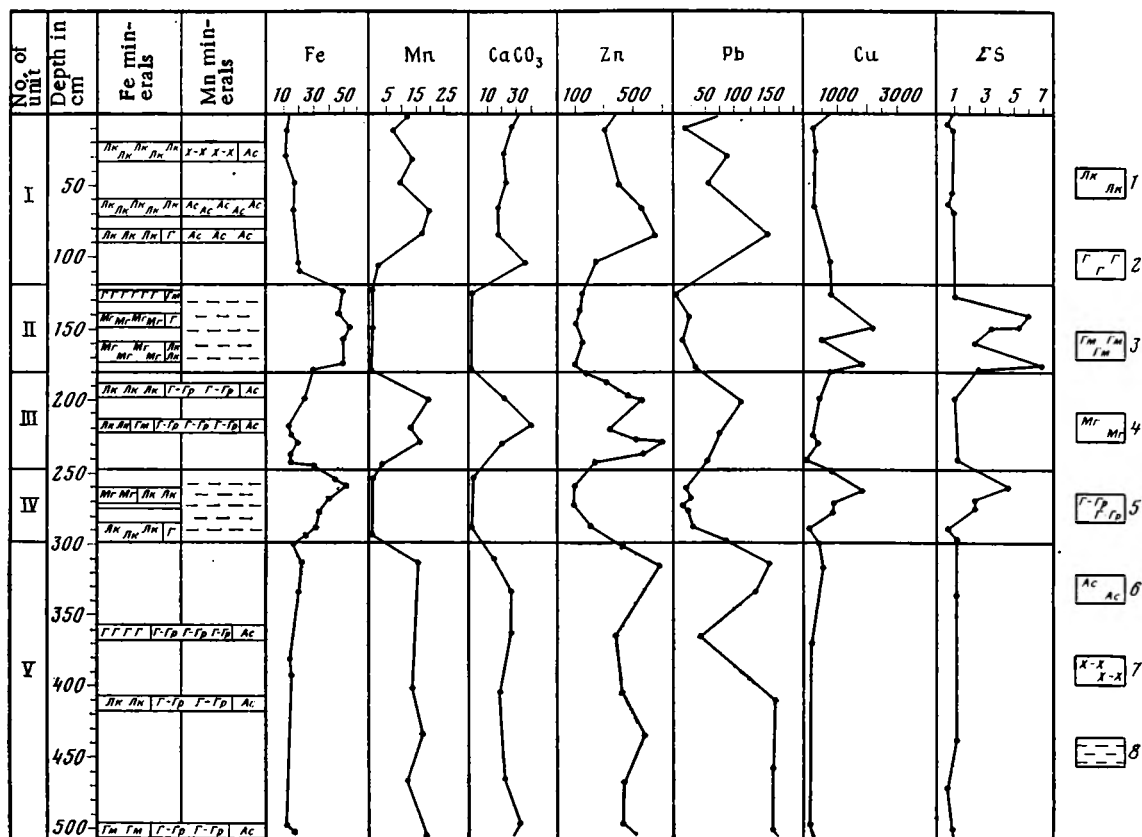


Fig. 6. Distribution of chemical elements and the basic iron- and Mn-oxide minerals in the Tethys Basin sediment sequence: 1) lepidocrocite; 2) goethite; 3) hematite; 4) magnetite; 5) goethite-groutite; 6) asbolites; 7) asbolitelike X-phase; 8) no minerals. The Fe, Mn and CaCO_3 content and total-S given in percentages. Zn, Pb and Cu content given in 10^{-4} %.

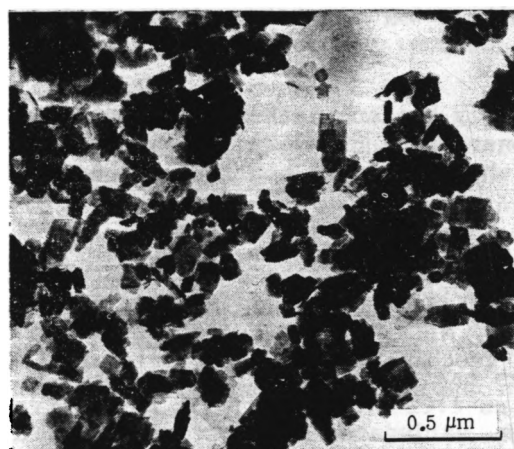


Fig. 7. Electron-microscope image of goethite-groutite particles from sediments of the Tethys Deep (station 224; 500-510-cm interval).

5-22% Fe = 14-24%; Fe/Mn: 0.8-1.09). These horizons typically contain no easily soluble Fe(II)-forms or significant amounts of mobile Mn(IV). In contrast with horizons II and IV, the sediments are relatively enriched in Zn and depleted in Pb (Fig. 6).

Detailed study of 13 samples from the investigated core, by the discussed complex of methods led to the identification and characterization of the iron- and manganese-oxide min-

eral complex in the sediments, the review of their areal distribution and description of their mineralogy, in comparison with the minerals of the Atlantis-II Deep.

Iron Oxides and Hydroxides. The following iron oxide minerals were identified in the sediments of the investigated section: magnetite, goethite, hematite and lepidocrocite. Their quantities and mutual relationships indicated regularly changing patterns, in relation to the rhythmic layering of the previously discussed ore beds. Lepidocrocite and magnetite were the most typical iron minerals in the studied sediments.

γ -FeOOH lepidocrocite was unevenly distributed throughout the entire section. It was most abundant in the upper parts of the section (unit I), where it alone represented the iron phase. In the other horizons it occurred in combination with other iron oxide minerals; goethite and magnetite (units II and IV), hematite and goethite (unit III), and goethite (unit V).

Magnetite occurs only in iron ore horizons II and IV. It is closely associated with layers, enriched in Cu and S (Fig. 6). The mineral is very unevenly distributed in the sediments; usually it forms finely dispersed microimpregnations, also fine laminae and lenticular concentrates, oriented parallel with the layering. These concentrates display a sooty-black color. Magnetite usually occurs as well-defined crystals, several hundredths of mm in size; also as finely dispersed powdery matter and in shapes of colloidal blobs.

Hematite occurs only in small quantities in individual horizons (units III and V), usually in combination with goethite-groutite.

As an independent mineral phase, goethite was recognized in individual samples within the iron ore unit. Usually it occurs in Mn-rich sediments as goethite-groutite, represented, as in the Atlantis-II Deep, by short columnar, tabular microcrystals of 0.1-0.15 μ m size (Fig. 7).

Thus the associations and quantitative relationships of the Fe and Mn-oxide minerals in the Tethys Deep deposits differ significantly from those of the Atlantis-II Deep. The greatest difference involves the widespread distribution of lepidocrocite in the Tethys Basin, the presence of large quantities of magnetite in certain parts of the section and the lesser amounts of hematite and monomineralic goethite. Goethite-groutite is most typical of the lower part of the section. Ferrihydrite, present in the Atlantis-II Deep sediments, was absent from those of the Tethys Basin.

Mn-Oxides and Hydroxides. The Mn-oxide and -hydroxide phases in the Tethys Deep differ sharply from the mineral association in the Mn-ore layers of the Atlantis-II Deep sediments. While the Atlantis-II minerals are primarily represented by minerals with tunnel-structures (todorokite and manganite), the investigated Tethys Basin samples contain layer-structured Mn-hydroxide.

Mixed-layer phase asbolites were the most widespread Mn-minerals in the Tethys Deep sediments. Their structures display alternating layers that include a different type of (001) plane. The asbolites appear as lamellae in the EM images (Fig. 8a). In agreement with results of electron dispersion analyses, the asbolites, in addition to the predominant Mn, also contain Al, Mg, and Ca (Fig. 8b). The asbolites often form ultrafine growths with layer silicates.

The asbolite electron diffraction patterns (Fig. 8c) include two hexagonal reflection sets, typical of these minerals. These reflections characterize the mineral sublattice as possessing a -values of 2.85 and 3.02 Å. The data indicate that the mineral contains two types of octahedral layers. The first one contains Mn^{4+} as the basic cation; the second, Mn^{3+} , and also Al, Mg and Ca. The absence of the first basal reflection $d = 9.6$ Å from the electron pattern, obtained from the recurved margins of asbolite particles indicates that layers of these two types alternate in a disordered fashion within the structure of the mineral [8].

One of the sediment horizons for the very first time yielded a Mn-asbolite phase, provisionally named here the X-phase. The particles of this phase had lamellar shapes (Fig. 8d) and, according to the energy dispersion analyses, displayed a strong predominance of Mn. Electron patterns of the X-phase (Fig. 8e) represent the superposition of three hexagonal reflection sets with strictly defined orientation directions, with respect to each other. These differ in their varying distances from the center of the electron pattern. The three reflections, closest to the center, corresponded to interplane distances $d = 2.49, 2.60,$ and 2.72 Å; those with the greatest distance from the center displayed values of $d = 1.44, 1.50,$ and 1.57 Å.

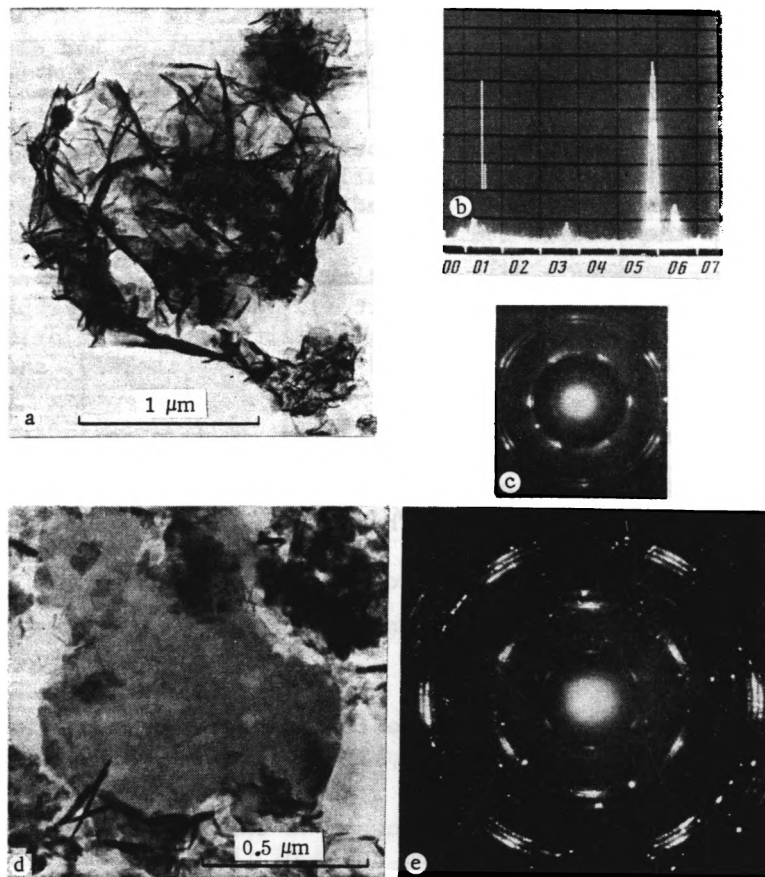


Fig. 8. Electron-microscope images, electron-diffraction patterns, and energy dispersion spectra of Mn-oxide phases from sediments of the Tethys Deep. a) aggregate of lamellar asbolite particles (225-235-cm interval); b) energy dispersion spectrum of asbolite particles; c) electron-diffraction pattern of asbolite particles; d) aggregate of particles of the asbolite-like phase X (20-35-cm interval); e) electron diffraction pattern of particles of phase X.

If one considers that the three hexagonal electron reflection sets correspond to the three hexagonal sublattices of the mineral, it may be assumed that the structure of the X-phase developed through the combination of alternating or epitaxially growing three types of a -c layers, in disproportionate planes that differ in the basal a -parameter values. By measuring the inter-layer spacing, the a -parameters of the hexagonal sublattices of the three layer types were calculated as 2.88, 3.0, and 3.14 Å. The diffraction and energy dispersion data may be best explained by the fact that the X-phase includes layers of the three types that either irregularly alternate within the individual microcrystals, or form submicroscopic growths. The various values of the a -parameter may be explained if the various layer types include a predominance of the Mn^{4+} , Mn^{3+} , and Mn^{2+} cations, correspondingly.

Goethite-groutite was the third Mn-bearing mineral in the ores of the Tethys Deep sediments. Particles of this mineral occasionally form practically monomineralic concentrates (Fig. 7).

The Mn-minerals in the Tethys Deep sedimentary sequence show a very regular distribution pattern. Thus, the X-phase occurs only in the topmost 20-35-cm interval of the investigated upper horizons. Asbolite, of a low level of structural ordering and predominant in Unit I, was found to a depth of ~ 1 m. Below ~ 2 m depth, the degree of the mineral's structural ordering increased in the lower sediment deposits, but its concentration values were very low. Goethite-groutite remained the predominant Mn-phase.

A broad complex of Fe- and Mn-hydroxides and oxides have been identified and described; their composition, parageneses and distribution patterns within the sections displayed great differences between the Tethys and Atlantis-II Basins.

In the second part of this paper we will attempt to analyze the formation conditions and mechanism of these mineral phases, in relation to specific depositional conditions and regimes of ore-forming processes in each of the basins.

LITERATURE CITED

1. J. Bischoff, "Sediments of Red Sea geothermal brines," Mineralogy, Chemistry and Genesis. in: Recent Geothermal Ore Deposits [Russian translation], E. Degens (ed.), 157-194, Ross, D. M. M., Mir (1974).
2. G. Yu. Butuzova, "Mineralogy and certain genetic aspects of metal-bearing Red Sea deposits. Part I," *Litol. Polezn. Iskop.*, No. 2, 3-23 (1984).
3. G. Yu. Butuzova, "Mineralogy and certain genetic aspects of metal-bearing Red Sea deposits. Part II," *Litol. Polezn. Iskop.*, No. 4, 11-32 (1984).
4. G. Yu. Butuzova, "Characteristics of hydrothermal-sedimentary ore formation in the Red Sea rift zone," *Litol. Polezn. Iskop.*, No. 5, 39-55 (1985).
5. F. V. Chukhrov, L. P. Ermilova, B. B. Zvyagin, and A. I. Gorshkov, "Basic data on ferrihydrite," in: *Hypergenic Iron Oxides in Geological Processes* [in Russian], Nauka, Moscow (1975), pp. 33-42.
6. F. V. Chukhrov, A. I. Gorshkov, V. A. Drita, et al., "Structural varieties of buzerite," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 10, 65-74 (1984).
7. F. V. Chukhrov, A. I. Gorshkov, V. A. Drita, et al., "Structural varieties of todorokite," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12, 61-71 (1985).
8. F. V. Chukhrov, A. I. Gorshkov, V. A. Drita, et al., "Mixed layer asbolite-buzerite minerals and asbolites in oceanic Fe-Mn-concretions," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 5, 91-100 (1983).
9. H. Bäcker and H. Richter, "Die rezente hydrothermal-sedimentäre Lagerstätte Atlantis-II-Tief im Roten Meer," *Geol. Rundschau*, Bd. 62, 697-741 (1973).
10. R. Bignell, D. Cronan, and J. Tooms, "Red Sea metalliferous brine precipitates," in: Strangway, D. (ed.), *Metallogeny and Plate Tectonics*, Geol. Assoc. Can. Spec. Paper, No. 14, 147-179 (1976).
11. J. Hackett and J. Bischoff, "New data on the stratigraphy, extent and geologic history of the Red Sea geothermal deposits," *Econ. Geol.*, 68, No. 4, 553-564 (1973).

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A set of crystallochemical methods has been used in a study of hard-to-diagnose alumophosphate minerals in bauxites from Middle Timan. The study established that alumophosphate in bauxite ores are represented by *svanbergite*, *goyazite*, and *crandallite*. Characteristic diffractograms and thermal analysis curves have been obtained for these minerals. Based on quantitative phase investigations, a *svanbergite*-*diaspore* ore variety has been identified in this deposit. Preliminary conclusions are drawn concerning the genesis of alumophosphates in bauxites.

Alumophosphates (*crandallite* and *goyazite*) were first discovered as rock-forming minerals of the bauxite-bearing strata by Krylov in the Zaostrov deposit (personal communication, 1980). Repina [7], studying the mineralogic and geochemical zonality of the productive bed, discovered that, besides *crandallite* and *goyazite*, phosphate-bearing argillites and bauxites contain large amounts of *woodhouseite*. Discrepancies in determinations of mineral forms of phosphates by different investigators are due to difficulties of identifying these minerals by any single mineralogic method. A correct analysis of the mineral composition of bauxites is needed not only for assessing the industrial properties of the ore but also for understanding the genesis of bauxites in this deposit. For this purpose, it was necessary to use a combination of physical-chemical methods to study the mineralogy of alumophosphates in the ore-bearing strata.

The deposit belongs to the basin type; it stretches and subsides gradually in the southeasterly direction, in conformity with the Riphean rocks [9]. At the base of the bauxite bed, one often finds clay-phosphate breccias, which are replaced up the section by pelitic rocks of an alumophosphate-kaolinite and bauxite compositions. Bauxites were formed as a result of lateritization of deluvial-proluvial redeposition products of marl and phosphate schist crusts of weathering of a Riphean age [8]. Relicts of such crusts of weathering, up to 4 m thick, have been preserved along the western outline of the deposit and are characterized by a kaolinite-frankolite-chlorite-sericite composition.

In the productive bed section the boundary of phosphorite and bauxite horizons is not discernible visually; it is drawn on the basis of chemical analysis. Bauxites appear as green-gray, less often red, loose clayey and rocky varieties (the latter are predominant). Alumina content varies from 43 to 46%; the average silicic modulus is 4.

Sections with the red bauxite-bearing sediments (eastern ore body) that had only been preserved in the southeastern extremity of the deposit exhibit a mineralogic zonality with a progressive increase of kaolinite and diaspore contents up the section — these are typical products of Devonian laterite weathering. The weathering of fluorapatite in such rocks is associated with a drop in P_2O_5 content; some of it is fixed in *goyazite* and, to a lesser degree, in *crandallite*.

Most bauxites are gray or greenish-gray, reflecting their burial in swamped territories [7]. This fact is also responsible for secondary (porous, crustificational, etc.) textures in the bauxites, consisting of aggregates of secondary minerals, mostly *chamosites*, alumophosphates, and *siderites*. In the chemical composition of these bauxites P_2O_5 content rises from 1 to 9%, FeO from a fraction of a percent to 12%, and CaO from 0.5 to 4%, with a deterioration of ore quality.

Phosphorous minerals in bauxites are found in close aggregates; they associate with *diaspore*, *chamosite*, and kaolinite, making it difficult to distinguish these phosphates in polished sections.

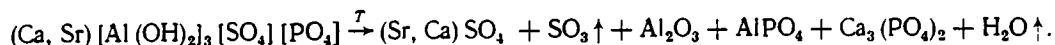
All-Union Institute of Mineral Resources, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 36-43, July-August, 1988. Original article submitted December 4, 1985.

For this reason, it was only with a combined investigation of phosphate minerals by x-ray, thermal, and chemical methods that we could determine with confidence *svanbergite* $\text{SrAl}_3(\text{SO}_4)(\text{PO}_4)(\text{OH})_6$, *woodhouseite* $\text{CaAl}_3(\text{SO}_4)(\text{PO}_4)(\text{OH})_6$, *goyazite* $\text{SrAl}_3(\text{PO}_4)(\text{HPO}_4)(\text{OH})_6$, and *crandallite* $\text{CaAl}_3(\text{PO}_4)(\text{HPO}_4)(\text{OH})_6$ in the rocks of this deposit.

A study of 27 natural specimens and 11 technological samples from various bauxite fractions was conducted with a thermoflex thermoanalyzer, a Q-1500D derivatograph, and a DRON-3 x-ray diffractometer.

The x-ray diffractometric characteristic and the data of chemical and thermal investigations placed the phosphate minerals of the bauxites tentatively in subgroups of sulfate-phosphates and aluminum phosphates of the alunite group [4]. The minerals of these subgroups are structural analogs and belong to ditrigonal-scalenohedric symmetry type with the spatial group $\text{R}\bar{3}\text{m}$. Isomorphism in the cation component (Ca, Sr, Ba, etc.), typical for these minerals [1], gives rise to continuous isomorphic series with the variation of the parameter c [9]. The similarity of unit cell parameters is responsible for similar sets of diffractive reflections. The only exception is the reflection from plane (131), which is the most intense characteristic reflection; it varies from one mineral to another in the interval of d of 2.97-2.94 Å [2]. The specimens were divided into two groups: one group (six specimens) had diffractograms with a single intense reflection $d = 2.95$ Å; the other group (31 specimens) had two intense reflections $d = 2.97$ and 2.94 Å, with intensity ratios ranging from 1.9 to 2.7 (Fig. 1). The characteristic set of diffractive reflections and the heightened content of SrO , SO_3 , and CaO in group I (see Table 1) suggest that they contain *svanbergite* similar to *svanbergite* from the Aturkol massif in the southeastern Altai Mountains [6]. Most specimens (group II) displayed two reflections in the 2θ angle interval of 37-40° (FeK_α) and variations of intensities of these reflections, suggesting mixes of phosphate minerals that prevent their reliable identification.

Thermal investigations were mainly based on differential thermal analysis (DTA) and thermogravimetry (TG). A study of the thermal decomposition of the fraction with a high content of alumophosphate minerals combined with x-ray phase investigation suggested that the decomposition process can be described by the following formula:



The DTA curves of specimens of group I (Fig. 2a), as determined by x-ray patterns, exhibited thermal effects typical for alumophosphates: 1) endothermal with T_{max} , varying in the interval of 630-640°C associated with dehydroxylation and amorphization of alumophosphate minerals; 2) exothermal effect with T_{max} shifted from 910 to 945°C, associated with crystallization of the amorphous phase; and 3) endothermal effect with $T_{\text{max}} = 1050-1100^\circ\text{C}$ due to decomposition of the sulfate complex.

In group I specimens we have obtained for the first time the curves of differential thermal analysis of minerals of the *svanbergite*-*woodhouseite* series with a composition close to that of *svanbergite*. Two specimens of the group (site 5146, specimen 23; site 131, specimen 4), which contained minor amounts of *chamosite*, were studied in a quasiisothermal-quasiisobaric regime. Based on the resolution of the intervals on the TG curve of the weight variation of diaspore and alumophosphate-sulfate due to loss of water and hydroxy groups, we determined that the content of minerals similar to *svanbergite* in specimen 23 was 24.5% and in specimen 4 32%; the contents of diaspore were 66.6 and 29.3%, respectively.

DTA curves of group II (Fig. 2b, c) display two or three endothermal effects in the temperature interval 535-640°C due to dehydroxylation of alumophosphate minerals (*woodhouseite*, *crandallite*, and *goyazite*); two exoeffects with T_{max} shifted from 870 to 885 and from 910 to 965°C, reflecting the formation of new phases; and a single endoeffect in the interval of 1000-1150°C, reflecting the decomposition of the sulfate complex of these minerals. Since neither x-ray patterns nor thermal investigations diagnosed reliably the phosphate varieties of alunite type in group II, we investigated their concentrated fraction (specimen 132-13). From alumophosphate nests we separated with a sieve the fraction of 0.25 mm and by roiling of clay minerals accumulated a concentrated material with a high content of alumophosphate minerals. The diffractogram of this concentration fraction, unlike that of the primary specimen, had a lower intensity of peaks ($d = 5.72$ and 2.97 Å); the reflection with $d = 2.28$ Å typical for *crandallite* was absent (see Fig. 1b, c); this mineral was removed with the clay fraction by roiling. The heating curve of the fraction (see Fig. 2d) displayed two endoeffects, with $T_{\text{max}} = 530^\circ\text{C}$ and a much greater effect with $T_{\text{max}} = 580^\circ\text{C}$, and two exoeffects at 850 and 985°C.

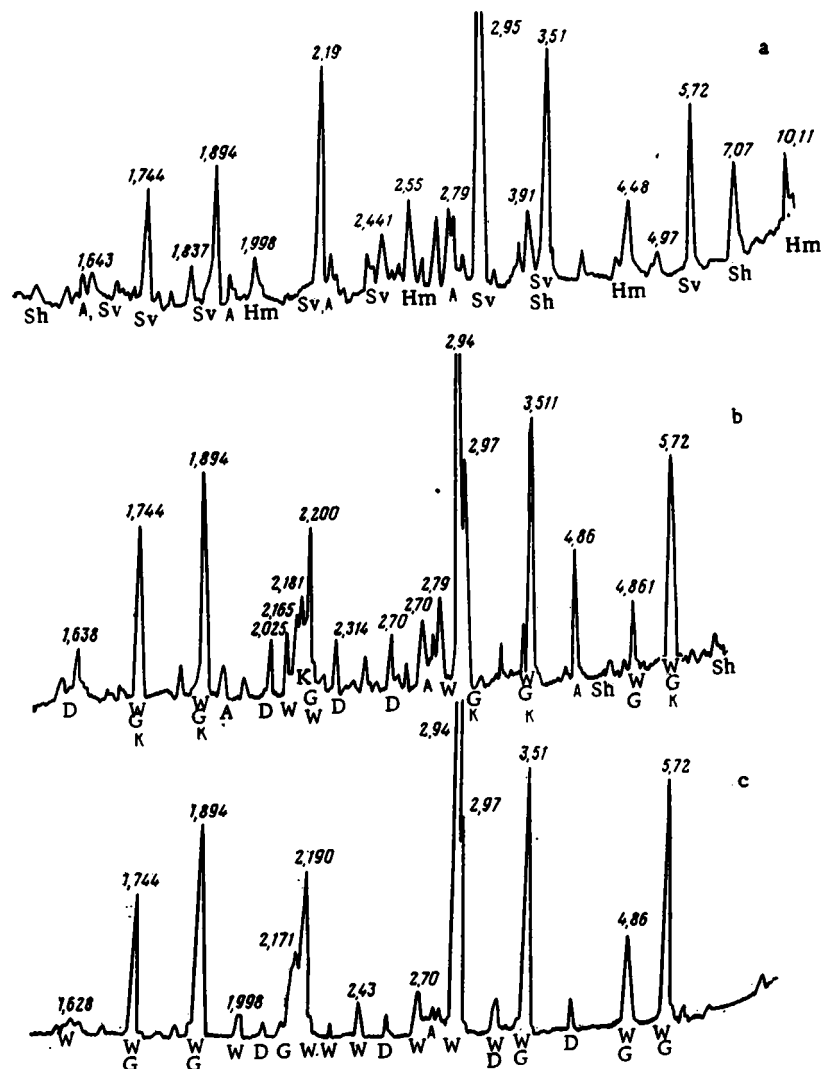


Fig. 1. Diffractograms of alumophosphate-diaspore bauxites: a) specimen 5146/17 (group I); b) specimen 132/13 (group II); c) fraction enriched in alumophosphate minerals (specimen 132/13); A = apatite; W = woodhouseite; G = goyazite; Hm = hydromica; D = diaspore; K = crandallite; Sv = svanbergite; Sh = chamosite.

The thermogravimetric curve showed a total weight loss of 17.3%, which corresponds to the sum of released water (16%) and sulfuric anhydride (1.3%). The low content of the sulfuric anhydride is explained by the fact that some of the sulfur from phosphate minerals was bound in cakes [5]. In order to verify this, a second heating of this fraction was conducted, where DTA (see Fig. 2e) showed two reversible endothermic effects with $T_{\max} = 1130$ and 1170°C , corresponding to polymorphous transformations of CaSO_4 and SrSO_4 [3].

The chemical composition of the fraction was the following (%): Al_2O_3 34.94; CaO 9.29; P_2O_5 23.80; SrO 6.60; SO_3 1.3; H_2C 16; BaO 0.22; others 7.65; $\Sigma 99.8$.

The study by this set of methods thus determined that the concentrated fraction (specimen from group II) consists of a calcium phosphate-sulfate (woodhouseite) and strontium phosphate (goyazite); judging by the intensities of diffractive reflections and the intervals of weight variation on the TG curve, the amount of woodhouseite is approximately twice that of goyazite.

Studies of specimens of group II in quasiisothermal-quasiisobaric conditions indicated that the TG curve does not provide a complete resolution of weight variation intervals, making it difficult to exactly calculate the quantities of each of the alumophosphate minerals. In some of the specimens of group II the total quantity of these minerals determined by the amount of water released in TG curves can be as large as 30%.

TABLE 1. Chemical Composition and Thermal Effect Temperatures of Phosphate-Bearing Bauxite Rocks with Characteristic Spacings of Sulfate-Phosphate and Aluminum Phosphate

Group	Specimen number	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	FeO	TiO ₂	P ₂ O ₅	CaO	MgO	SrO	BaO	SO ₃	Loss to annealing	Σ	Temperature of maximal effect, °C		d (101; 110; 113; 122; 107; 033; 303; 220), Å
															endoeffect	exoeffect	
I	131/4	38,1	11,8	1,9	4,0	1,4	11,2	6,1	2,0	5,4	0,1	3,5	14,7	100,2	535, 630, 1100	910	5,72; 3,51; 2,95; 2,44; 2,190; 1,894; 1,744
	5146/17	26,2	24,5	3,6	3,8	1,7	10,3	7,4	1,4	5,6	0,1	3,7	12,2	100,5	635, 1055	945	
	5146/23	61,6	2,3	2,9	0,7	3,1	5,0	1,1	0,4	3,8	0,3	3,5	15,6	100,3	545, 640, 1100	940	
II	130/6	38,4	9,6	4,0	7,6	1,1	11,4	4,8	4,2	2,9	0,1	1,8	14,6	100,5	545, 630, 1080	870, 940	5,72; 3,51; 2,97; 2,94; 2,190; 2,171; 1,894; 1,744
	130/7	38,5	11,0	1,6	5,4	1,7	14,5	6,6	2,8	2,8	0,2	1,9	13,4	100,4	545, 635, 1070	875, 955	
	132/13	33,2	6,9	1,3	Not found	1,7	20,0	15,0	1,5	3,2	Not found	3,4	12,2	99,8	535, 570, 630, 1110	845, 955	5,72; 3,51; 2,97; 2,94; 2,200; 2,181; 2,165; 1,894; 1,744
	610	38,4	13,4	9,1	—	Not found	11,4	4,2	Not found	3,9	»	Not found	—	—	535, 575, 620, 1020	890	

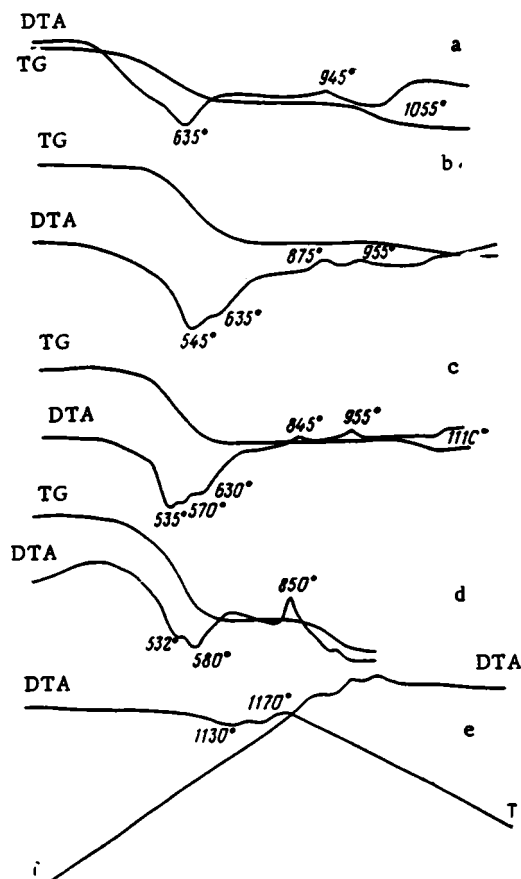


Fig. 2. DTA and TG curves of alumophosphate-diaspore bauxites: a) specimen 5146/17 (group I); b) specimen 130/7 (group II); c) specimen 132/13 (group II); d) fraction enriched in alumophosphate minerals (specimen 132/13); e) alumophosphate mineral fraction after double heating (specimen 132/13). Microphotography of alumophosphates in bauxites.

The diffractograms of specimens of group II were used to select for thermal analysis a high-crandallite specimen. A study of the thermal decomposition of crandallite from the Zao-strov deposit showed that it had an endothermal effect with $T_{\max} = 630^{\circ}\text{C}$ and an exothermal effect with $T_{\max} = 995^{\circ}\text{C}$ (see Fig. 2c).

With the exact diagnosis of phosphate minerals it was possible to describe the segregation patterns and crystal morphology in the ores of this deposit.

Goyazite in polished sections appears as crystal aggregates growing after fragments of an apatite composition. Fragment contours nearly blend with cement and can be barely discerned in crossed nicols of the microscope; they resemble nests filled with colorless crystals. Crystallization of goyazite involves a change of segregation from cryptocrystalline through isometric to well-faceted crystals with an orthogonal rhombic cross section, ranging in size from 0.1 to 0.025 mm (Fig. 3a, b). Goyazite grains have poor pleochroism and exhibit a high relief and low birefringence.

Crandallite is segregated in rocks similar to goyazite, forming fragments of a goyazite-apatite composition surrounded by a brown rim. The contour is sometimes partially preserved, and fragments have "blurred" outlines (see Fig. 3c). The crystals are of a pseudocubic habitus and range in size from 0.015 to 0.02 mm, with some individuals as large as 0.02-0.07 mm; they are colorless and transparent, with perfect cleavage and direction extinction; the birefringence is low.

Woodhouseite forms continuous cryptocrystalline yellowish masses developed both after goyazite-crandallite fragments and after kaolinite-hydromica cement. In massive segregations, sinters, and clots it associates closely with chamosite and diasporite. Small bud-like units

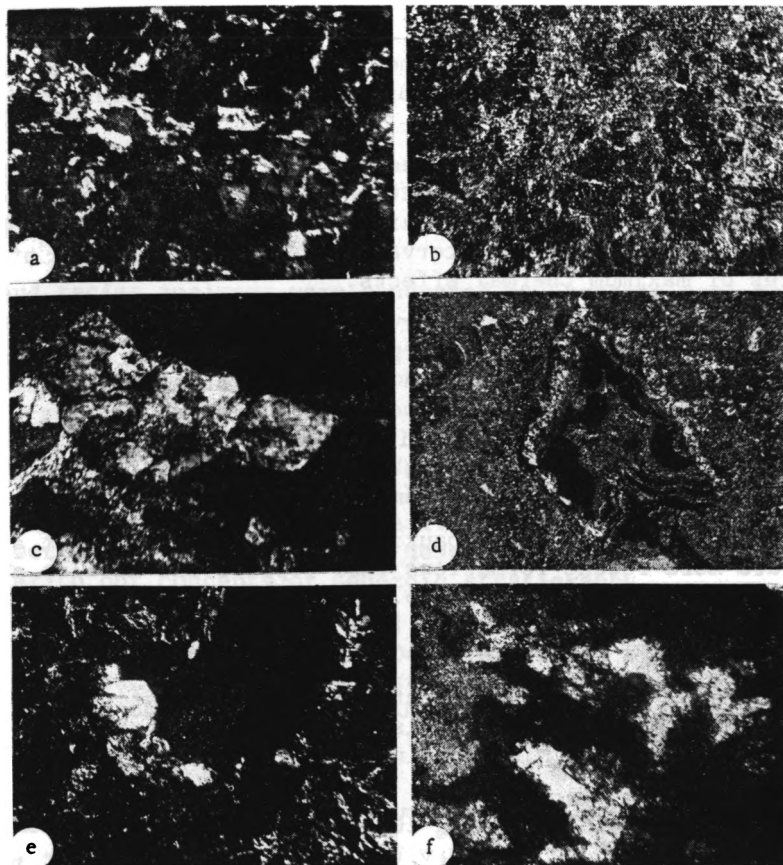


Fig. 3. a) Goyazite crystals in phosphate-kaolinitic argillite (polished section, magnification $\times 175$, crossed nicols); b) fragments of an apatite composition replaced by microcrystalline goyazite (polished section, magnification $\times 25$, parallel nicols); c) crandallite crystals in a cavity in alumophosphate-kaolinitic argillite (polished section, magnification $\times 175$, parallel nicols); d) budlike woodhouseite units in bauxite (polished section, magnification $\times 39$, parallel nicols); e) a cavity in bauxite covered with woodhouseite crystals (polished section, magnification $\times 175$, parallel nicols); f) pores in bauxite rimmed by svanbergite crystals (polished section, magnification 175, parallel nicols).

of a zonal composition from 0.1 to 0.2 mm are typical; they have a cryptocrystalline and spherulitic structure of the outer zone, consisting of columnar or prismatic woodhouseite crystals (see Fig. 3d). Holocrystalline varieties are also found in veinlet-like segregations, where woodhouseite appears as prismatic (0.02×0.01 mm) or columnar (0.01×0.08 mm) crystals which are colorless, with cleavage and high relief, and interfere with gray tones (see Fig. 3e).

Svanbergite in bauxites and bauxitic rocks, like woodhouseite, is found mainly in cryptocrystalline (less often in microcrystalline) states. The constant occurrence of svanbergite in rock fragments and cement and its association with chamosite, diaspore, and finely dispersed organics indicate a mainly authigenic origin. Cryptocrystalline svanbergite almost does not react with polarized light and has an average light refraction of 1.630-1.640. Microcrystalline svanbergite fills pores. Depending on faceting, crystals are shaped as lenticular or rhombic tablets, less often forming columnar crystals of 0.006-0.017 mm (see Fig. 3f). The largest individuals are up to 0.02-0.03 mm in size. The crystals are colorless, with direct extinction $n_e - n_o = 0.01$. Genetically, these phosphates are inhomogeneous. Goyazite and crandallite are of a possible lateritic origin, suggested by their segregation as substitution aggregates developed after apatite fragments. The predominant form of segregation of woodhouseite and svanbergite in this deposit is as solid masses of veinletlike or budlike units developed after goyazite and crandallite; they are probably of an epigenetic origin.

The following conclusions have been drawn from this investigation.

1. It has been established for the first time that alumophosphate in Zaostrov bauxites belong to subgroups of sulfate-phosphates and aluminum phosphates, represented by svanbergite, crandallite, woodhouseite, and goyazite.

2. It was possible to diagnose phosphate minerals precisely only by using a combination of crystallochemical methods, mainly x-ray diffraction and thermal investigations. For the first time, diffraction reflections have been obtained for each of the phosphate minerals of this deposit. DTA curves determined the intervals of dehydroxylation of each of the minerals and the temperatures of maximum thermal effects.

3. Based on derivatographic recordings under quasiisothermal-quasiisobaric conditions, it has been established that the amount of svanbergite in some of the specimens is high, making it a rock-forming mineral. A svanbergite-diaspore variety of ore can thus be identified in this deposit. The more widespread varieties are woodhouseite-diaspore ores with goyazite and crandallite, because most bauxite specimens contain these minerals with a total quantity of up to 30% in some specimens. It has been established that among minerals of the alunite group the minerals of the sulfate-phosphate aluminum subgroup are predominant in these ores.

4. A petrographic study of bauxites and bauxitic rocks has shown that aggregates of sulfate-phosphate minerals are more recent formations that replace and develop after aggregates of the minerals of the aluminum phosphate subgroup.

LITERATURE CITED

1. Z. S. Altshuler, Phosphorus in the Environment [Russian translation], Mir, Moscow (1977).
2. E. K. Vasil'eva, Radiometric Index of Minerals [in Russian], Nauka, Moscow (1974).
3. V. P. Ivanova, Thermal Analysis of Minerals in Rocks [in Russian], Nedra, Leningrad (1974).
4. M. A. Kashkai, "The alunite group and its structural analogs," Zap. Vsesoyuz. Mineral. o-va, Ser. 2, 98, No. 2, 150-162 (1969).
5. M. A. Kashkai, The Alunite Group and Its Structural Analogs [in Russian], Élma, Baku (1977).
6. E. I. Nikitina, A. P. Berzina, I. K. Kuznetsova, and V. I. Sotnikov, "Svanbergite in the Altai Mountains," Dokl. Akad. Nauk SSSR, 149, No. 4, 942-944 (1963).
7. M. N. Repina, "Bauxites of the northern part of the Middle Timan," in: Forecasting of Bauxite Deposits [in Russian], Nedra, Moscow (1983), pp. 42-55.
8. Yu. K. Krylov, "Middle Devonian high-phosphate bauxites of the Middle Timan," in: Bauxites and Other Ores of Aluminum Industry (Proceedings of a National Conference, August (1985) [in Russian], Savinskii, (1985), pp. 59-61.
9. R. S. Gilkes and B. Palmer, "Synthesis, properties, and dehydroxylation of members of the crandallite-goyazite series," Miner. Mag., 47, No. 2, 221-227 (1983).

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Paleobotanical and facies analyses were conducted on Cenozoic coal measures of the Far East. It was shown that the general evolutionary trend in morphostructures of the Khasan-Middle Amur zone and changes in content of the section are two criteria that suggest a higher stratigraphic position for the coal deposits.

An increased need for detail and reliability in stratigraphic differentiation on large scale geologic maps [31] calls for a renewed look at the stratigraphy of Paleogene-Neogene coal deposits of Primor'ie, which is far from ideal. The position of many stratigraphic units within the Cenozoic section is still debatable, despite the considerable progress of recent years in bringing order to our concepts of Cenozoic stratigraphy.

In the early 1960s, Gromov and Gromova [21] came out with a synthesis of the stratigraphy of Tertiary coal deposits of Primor'ie. They were able to show a pattern in the change of continental facies in the section from southwest to northeast, i.e. along the strike of the fold belt; marine limestones occur only on the Korean peninsula. Along this trend, from Pos'et to the lower reaches of the Bikin River, they noted a shortening of the younger part of the section resulting from the development of a system of intermontane depressions: the downwarps took place during the Paleocene in southernmost Primor'ie, and later involved adjacent areas, with maximum subsidence in the Oligocene to early Miocene, reaching western Sikhote-Alin to the lower course of the Amur River.

It is noted in passing that Varnavskii later arrived at nearly the same conclusion [14, 15], pointing out the variation in age of the commercial coal measures: Eocene in the Khasan facies, Eocene to early Oligocene in the Artemo-Tavrichansk basin, Oligocene in the Rakovsk basin, and early to middle Miocene in the Pavlovki, Shkotovsk, and Lower Bikin basins.

General information on the stratigraphy of coal deposits occurring in a large number of successive basins and grabenlike features has been published in a volume on the geology of the Primor'ie region [19]. According to widespread belief, emphasized in the volume, only the Paleogene deposits are coaliferous. The principle reserves of brown coal are Paleocene in age: middle Eocene (Nazimovsk and Maitunsk suites), late Eocene to middle Oligocene (Uglovsk suite and its correlatives), and Oligocene (Nadezhdinsk suite). Neogene deposits are considered to be coal-free; thin beds of lignite and clayey coal are disregarded.

We have carried out an analysis of a large amount of data on the geology and flora of coal measures of the Far East, using our own large paleobotanical collection obtained on visits to a great many coal localities [1, 2, 35]. We were able to introduce significant corrections in the problem of age and correlation: evidence was presented for coal deposits in both Paleogene and Neogene rocks. On the whole, in the scale of the deposition of the coal beds, the Cenozoic Epoch is one of major importance [29].

The view that commercial coals occur in the Neogene has now become generally accepted: Primor'ie coal measures (Khasan massif), previously referred to the Oligocene, have been transferred to the early to middle Miocene, "confirming the occurrence of Neogene coal resources throughout the southern Far East" [32, p. 170]. In [6], included in the summary of the Third Far Eastern Stratigraphic Symposium, the recognition of several stages of coal deposition in commercial thicknesses in the Cenozoic of Primor'ie: Eocene, Oligocene, and Miocene, is considered one of the principle accomplishments in the section on the Paleogene

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and Neogene. According to Varnavskii [16], the late Eocene to early Oligocene and early to middle Miocene are characterized by coal deposition.

This new material has clearly corrected many errors and misconceptions in the Cenozoic stratigraphic record, considering the relatively recent declarations that prospects were poor for fossil fuel resources in Tertiary rocks of Primor'e and the lower Amur River area. The Tertiary sequence, in the view of Rudich [33, p. 49], is composed solely of "continental volcanic formations with subordinate amounts of thin, coaly deposits."

The stratigraphic correlations adopted at the Third Far Eastern Stratigraphic Symposium for the Paleogene and Neogene of the onshore region of the Far East contain a number of errors which can be corrected only by a comprehensive, systematic approach to the study of the geological units. Clearly among the most pressing problems to be solved are the age and correlation of the volcanic and sedimentary rocks occupying the Khasan basin. However, the entire Khasan facies zone "is a key zone for development of the stratigraphy of the volcanic rocks in studies of then sedimentary and volcanic Paleogene... and Neogene sequence" [15, p. 29]. The correct resolution of the problem would reduce the impact of alternative concepts and would reinforce current views on the tectonic setting of coal deposition in terms of a combination of climatic, structural, and geomorphic conditions [26].

Information is often published on the geology of the Khasan basin, in southwestern Primor'e (around the town of Kraskino), which is included in the Pritumangansk group of basins that are widespread throughout Korea. The sequence of suites, from the base upward, is: Novopos'et, Nazimov, Zaisanovsk, Khasan (Uglosk), and clayey tuffite (Fatashinsk). Geologists almost unanimously assign these units to the Paleogene.

In general, sedimentation took place in a mobile, polyfacies setting with widespread volcanism. Alluvial channel deposits of mountain streams (Nazimovsk suite, basal Khasan suite) grade into swamp deposits (upper Khasan suite) followed by lake sediments (clayey tuffite suite, or in other interpretations, sequence).

Deposition of commercial coal sequences, including the Khasan, took place during rapid subsidence of the basin and uplift of the surrounding orogenic structures. The presence of finegrained clastics is explained by these contrasting morphostructural combinations [41]. Attention has been drawn to the presence of deep faults that trend northeast and north-south, which are characteristics of the coal basin [18].

We have discussed the geology and paleoflora of the Khasan coal measures in detail in earlier papers [2, 4]. Our treatment was as follows. The rocks of the Khasan basin, although quite variable in composition and thickness appear somewhat uniform in the broad sense of the word. There is a coal-bearing Khasan suite of Miocene age, which is generally subdivided into basal, coal-bearing, and supra-coal (clay-tuffite) parts. Establishment of these parts as independent suites is artificial and can be supported from neither a lithological nor paleobotanical viewpoint.

The treatment did not deal with the nomenclature system, which we will discuss later, especially with respect to the stratigraphic position of the clay-tuffite sequence crowning the Khasan coal section.

Flora of the clay-tuffite sequence is quite typical. More than half are thermophilic forms, represented at present by subtropical forests of Southeastern Asia. The main floral role is played by the beech association, represented by beech, chestnut, and oak. They are quite numerous. Beech trees, which indicate high elevation, are a landscape-shaping species, growing under conditions of broad, warm plains; they define the environment of the entire association, which (as in nearby mesophytic deciduous forests) is limited to 900-1000 m above sea level. The region as a whole is characterized by mountainous relief; depressions located around the mountains experienced extensive coal deposition.

This flora, known as Kraskino, was and is still considered Oligocene in age by the vast majority of investigators. It has been considered to range from middle Oligocene to middle Miocene only in [39]. Similar flora is found only in Korea. On this basis it has been included as a feature of Oligocene flora on the margins of the Eurasian continent. It is distinguished by a high content of narrow leaved oaks and chestnuts, which attracted the attention of Krishtofovich [25] in his studies of the flora of Novokievsk (now Kraskino), and bladed oaks of the type Quercus ussuriensis Kryshch.

The Kraskino flora has been determined to be Miocene in age, and such types should be sought among Miocene flora. Comparisons made by us have shown that numerous flora of Primor'e (Sinevo Utesa, Rettikhovki, Pavlovki, Amgu, Velikoi Kemi, Dembi) and northeastern Korea (Kogeonveon, Kungsim) are of the same age, fixing the climatic optimum of the Miocene at its final stage. Occupying a central position geographically, the Kraskino flora is like a connection between the Korean and Sikhote-Alin floras.

The floras above differ systematically in distribution. These differences result in an east-west zonation. These floras are closely related: they are associated in large communities of dominant families: Taxodiaceae, Fagaceae, Juglandaceae, Aceraceae. Clearly a strong argument in favor of this close relationship is the presence in these groups of such varieties as Styrax, Hamamelis, Mallotus, Zizyphus, Liquidambar, and Porana.

This association is emphasized by discovery in the Kraskino flora of Engelhardia koreanica Oishi [4], first established in Korea by Oishi [44] and later in Primor'e. This species is now reported in the Kogeonveon flora in the Khveam suite [39], otherwise known as the Engelhardia bed [43], which in Primor'e is the same age as flora of Rettikhovki, Velikoi Kemi, and Kemi [7]. The correlation of the Korean and Sikhote-Alin floras with Engelhardia is confirmed by modern studies [8].

Correlational difficulties remain. As a result of a resolution of the stratigraphic council [32], floras of Rettikhovki, Velikoi Kemi, and Dembi (with Engelhardia) have been compared to Japanese floras of the Daidzima type, which correspond to a climatic optimum at the end of early Miocene. These Sikhote-Alin floras, which occur in a tuff-diatomite sequence and the Kizin suite of the Prihankaisk horizon, have been correlated with flora of the similar Khamchzhin suite of the Kil'chzhu-Menchkhon basin in northeastern Korea. The Engelhardia bed of the Khveam suite in the Tumangan group of basins, generally identified with the Khamchzhin suite [39],* is found at the level of the upper Oligocene to middle Miocene, while the clay-tuffite sequence of Kraskino, at the Oligocene level.

It should be noted that the correlation of the Engelhardia beds of Korea with the clay-tuffite sequence (Fatashinsk suite) of Primor'e has never been in doubt [13, 43, 47].

Such little-debated allocation of monotypic floras to various chronologic levels (from Oligocene to middle Miocene inclusive) does not help to resolve correlation problems in the coal measures that are related to flora-bearing beds.

In principle, the incorrect allocation of strata in the correlation schemes of the Paleogene and Neogene is explained not only by the lack of a clear picture of the evolution of Far Eastern Tertiary floras. Data on comparison of evolutionary dynamics of the flora and climatic fluctuations with sedimentation (in this case, coal deposition) has remained hidden from view.

Thus, according to the approved scheme, the coal-bearing deposits of the Rettikhovki coal measures are subdivided into two independent, temporally consecutive stratigraphic units: a coal seam 35-40 m thick (lower half of lower Miocene) and a sequence of tuffaceous diatomite 30 m thick with numerous plant remains (upper half of lower Miocene to lower half of middle Miocene).

A similar procedure was followed with respect to the Pavlovkii coal measures (town on Novoshakhtinsk). The total thickness of the coal-bearing beds is 60-70 m. The lower coal part of the suite, with a 30-m bed of coal exposed at the base, is placed in the upper Oligocene, while the upper part of the suite, barren of coal but with the main plant assemblages, is lower Miocene.

Coal measures with coal beds of workable thickness in the Khasan coal section (Khasan suite) are referred to the Eocene, while the overlying clay-tuffite sequence with flora is placed in the Oligocene.

If we follow this construction, even without paying attention to the artificial contrast of the enclosing coal deposits that have been raised to the rank of independent stratigraphic

*Flora of the Engelhardia bed in Korea is compared to floras of the early phase of development of warm-weather Miocene floras of the Daidzima type, while the Khamchzhin relates to the late phase of development of this type of flora [8].

units, then we can conclude that there was a major epoch of coal deposition in Primor'e at the Oligocene-Miocene boundary, although located geographically only in the Rettikhovki and Khankaish groups of basins.[†]

This assumption is as yet poorly supported by the climatic conditions of this time interval. The connection between climate and lithogenesis is well known. The history of coal deposition through time has not been random, but has followed a pattern: it has been subject to certain laws dictated by an array of geologic conditions [11]. Accumulation of coal deposits is characterized by a warm, constantly humid climate. If the voluminous data on the climate of eastern Asia at the Oligocene-Miocene boundary is examined, this period of time is seen to be quite different: a cooling is found, and there is evidence that the Oligocene was the coldest epoch of the Paleogene [40, 45, 46]. This conclusion is derived from general information on Paleogene and Neogene flora of the middle and higher latitudes, provided by Akhmet'ev [5]: in east Asia, it consisted to temperate or moderately warm-weather forests.

The facts quite clearly indicate a cooling throughout Siberia and adjacent region at the end of the Oligocene to the beginning of the Miocene [12, 20]: its continentalization took place and its temperature regime changed temperature regime changed from warm temperate at the beginning of the Oligocene to temperate at the Oligocene-Miocene boundary. A distinct climatic change is observed in the central Para-Tethys: at this time Arcto-Tertiary elements became dominant, indicating climatic cooling and seasonal changes [42].

Thus, the conclusions that there was a warm humid climate, arrived at from an analysis of the lithologic section of the Primor'e coal measures (the presence of a weathering mantle at the base of the coal deposits and the great thickness of the coal beds), contradicts the conclusion reached by the stratigraphic commission that there was a "climatic minimum corresponding to the stage of maximum cooling... at the Paleogene-Neogene boundary" [32, p. 160].

The contradiction is readily removed placing the coal deposits of Rettikhovki, Pavlovki, and the similar Khasan facies zones as a higher stratigraphic level in the Miocene, as has been done in the case of the flora-bearing beds overlying them.

It is of interest in a discussion of this scheme to adduce the known calculations of the time of coal deposition. It has been established that the formation of superthick deposits (more than 16 m for brown coals), such as the commercial beds of Rettikhovki and Pavlovki, takes only a short amount of time in the macrocycle, (a few hundred thousand years), since the macrocycle, according to [22], takes two magnitudes of time longer for deposition of the coal-bearing sequence.

According to Varnavskii [16], an optimum condition for growth, accumulation, and preservation of plant material is the rapid subsidence of the basin, equal to 10-15 m/million yr. Even if neutral or clearly understated indicators of rate of subsidence are considered, the time of formation of the entire Rettikhovki, as well as Pavlovki, coal sequences could not exceed 5 million yr.

The correct solution of the problems of Paleogene-Neogene coal resources of Primor'e are impossible without thorough and systematic analysis of information in the Lower Bikin brown coal deposit, located in the northern region.

Unfortunately this information has only begun to be accumulated, consequently the level of stratigraphic and correlational synthesis remains low. In a comprehensive volume on the geology of the Primor'e region [19], only a schematic picture of the geology of the Lower Bikin basin is presented, amounting to a statement that the Oligocene coal-bearing sequence is here undivided. It is true that a different age of the coal-bearing sequence is presented in an appendix: the age range is provisionally expanded to include the Miocene. The geologic section of the basin has been presented schematically in an outline of the geology of Soviet coal deposits [27]; along with the vast Khabarovsk basin, the Bikin basin is categorized as neotectonic.

The coal measures, about 1800 m thick (based on geophysical data), are subdivided into three units (suites): a lower coal-bearing, a middle coal-free, and an upper coal bearing suite. They have been correlated with coal measures in the Middle Amur [24] or Uglovsk [38] basins.

[†]The Nealy Creek Formation in Alaska, along with its coals, is considered upper Oligocene (?)—lower Miocene [49]. Engelhardia flora is sparse and atypical. It has been suggested that in its type area this formation is early Miocene in age [48].

Like Paleogene deposits in southern Primor'e, deposits in the Lower Bikin area are generally subdivided into two suites: Uglovsk and Nadezhdinsk (with two subsuites). The Uglovsk suite and upper Nadezhdinsk subsuite contain coal beds of commercial thickness.

After revision of certain Tertiary floras of Primor'e (Rettikhovki and others, which indicate Miocene age but not Oligocene [32]), the stratigraphic position of floral horizons and associated coal measures were reexamined. The nomenclature in the area of the deposits was partially replaced. Following the new interpretation, the upper productive subsuite of the Nadezhdinsk suite was raised in rank to the Ust'-Davydovsk suite of Miocene age, and the name "Nadezhdinsk suite" was retained for the lower, nonproductive subsuite.

Doubt about the correlation scheme remains. First, the position of the Ust'-Davydovsk suite in the Cenozoic section is debatable. Second, the principal criterion for subdivision and age-dating is a lithologic feature: the coal content of the Paleogene Uglovsk suite. It is obviously risky to include, in the same stratigraphic unit, deposits formed in different facies zones.

The difficulty in correlating coal units in these deposits is the result of sparse data on the flora: the Bikin flora has been studied less than others. Information is generally limited to a list of species without accompanying descriptions. An exception is a brief communication [23], in which plant communities from various stratigraphic levels are presented and species are described from Ginkgo, Taxodium, Metasequoia, Glyptostrobus, Juglans, Betula, Ulmus, Zelkova, Cercidiphyllum, Liquidambar, Euonymus, Rhamnus, and Alangium.

On the basis of systematics, the flora is identified as of the Turgaisk type, and without a great deal of confidence, is assigned to the Miocene; an Oligocene age is not excluded. Consequently, there is no particular addition to the flora. Information on continental malacofauna [30] has so far contributed little to the resolution of the age problem.

The Far Eastern Stratigraphic Commission [32] has retained a threefold division of the sequence in the Cenozoic stratigraphy of the Bikin group of basins: an upper coal-bearing unit (Miocene), a coal-free unit (Oligocene), and a lower coal-bearing unit (Eocene-Oligocene; Eocene according to [10]).

Biostratigraphic study of the Lower Bikin deposit has been conducted by Ablaev since the middle 1970's [2, 3]. He was able to collect and study macrofossils from the upper coal-bearing unit of the area of the first Bikin deposit (near the town of Luchegorsk), where coal beds are currently being worked. This unit has a total thickness of 600-750 m and includes 15 groups of complex beds forming four coal-bearing horizons.

Plant-bearing beds occur above coal bed 3B, in the first coal-bearing horizon (beds 1-4), and are distinguished by a substantial thickness (30 m or more) and relatively widespread distribution.

The following species were identified: Metasequoia disticha (Heer) Miki, Glyptostrobus europaeus (Brongn.) Heer, Cercidiphyllum crenatum (Ung.) R. W. Brown, Alnus schmalhauseni Grub., Carpinus sp., Corylus kenaiana Hollick, Ulmus drepanodonta Grub., U. appendiculata Heer, Tilia praeamurensis Hu et Chaney, Acer amurense Pojark., Acer sp. 1, Acer sp. 2, Koelreuteria miointegrifolia Hu et Chaney, Populus balsamoides Goepp. (var. jarmolenkoi iljinskaja), Ampelopsis populifolia Hut et Chaney.

Also considered to be present were Viburnum, Catalpa, Vitus, Fraxinus, and Abronia. The systematic affinities of a number of samples remain obscure.

A birch (leaf) covering is dominant, composed of leaf impressions of Alnus pojarkovae.

Added to the floral spectrum are poplar and elm, counted in several tens of samples. Conifers, mainly Glyptostrobus, apparently play a high phytocenotic role as well. The remaining species are significantly reduced in relative amount; as a rule, they are found in two or three samples in a collection, and are not included in the category of landscape formers.

According to its bioecological type, the plant assemblage preserved belongs to an association restricted to gently sloping expanses, similar in ecological affinity and systematic structure to late Miocene Ust'-Suifunsk flora of South Primor'e [9]. It suggests flora typically limited to the Razdol'naya River basin. It is made of virtually the same

association at the generic level, giving the flora a certain aspect: Alnus, Betula, Populus, Carpinus, Salix, and several other taxa.

The plant collection is not so extensive as to give an unequivocal answer to the question of the age of the coal measures in the Lower Bikin basin. At the present stage of study of the flora, it is safe to accept a late Miocene to early Pliocene age, based on the overall composition of the flora and the evolution of enlightenment on the prevailing range of Tertiary floras of the Far East. In the succession of Neogene continental flora, it precedes the warmth-loving floras of the early Miocene of the Bolotninsk and Kraskino (Khasan) types [2]. Climatic conditions in Bolotninsk and Kraskino time favored the growth of a number of plants whose modern analogues are limited to the tropical belt of southeast Asia.

The Ust'Suifunsk, Botchinsk, and Lower Bikin flora of the upper coal-bearing unit reflect mainly the late Miocene stage of development of Far Eastern vegetation.

It is premature to consider the entire sequence late Miocene, since there is no paleontologic data on the lower productive unit. The remains of freshwater mollusks and Taxodia observed at this level are sparse, and are as yet not of use in age determination.

Moreover, at the current level of study the three units, which formed during a single major sedimentary cycle, should be considered to rank as the Neogene Luchegorsk series [3].

Hypotheses expressed on the higher stratigraphic level of the coal-bearing units to a certain degree are confirmed by an analysis of the entire morphostructure of the Khasan-Middle Amur rift zone and of the trend of change in content of the section.

The morphostructures of the Cenozoic tectonic and magmatic activity in eastern Eurasia are quite widespread. They are characterized by both genetic and morphologic diversity. Cenozoic basins are traditionally associated with regional and transregional linear morphostructures: zones of deep faulting. However, enough data have now accumulated to confirm that many other basins are also closely associated with central type morphostructures (CTM) of various orders (Fig. 1). In the region under consideration the predominant morphostructures are dome and dome-ring CTM, which in many Cenozoic basins are the curved or radial elements [37].

Figure 1 thus shows the basic CTM which are associated with Cenozoic depressions and volcanic structures. Some of these have been described earlier [37]. Correlation of time and space in the formation of the depressions and their filling with sediments, undertaken for the first time, has been conducted with a view to the mechanism of formation of CTM [37].

The association of Cenozoic extensional structures with magmatic dome and dome-ring morphostructures requires a more careful treatment of the methods of correlation of terrigenous sequences by lithologic features alone, when it is realized that coal-bearing and coal-free units are synchronous throughout the sequence [19]. Widespread lateral and vertical migration of zones with various depositional environments associated with the appearance of volcanism, initially basaltic and andesitic, should apparently be expected as indicating the presence of extensional conditions, which are most favorable for the formation of depressional morphostructures.

A number of CTM occur along one or both sides of depressional morphostructures, filled with volcaniclastic and terrigenous deposits. The greatest thicknesses of these deposits occur in structures located along the periphery of a number of CTM; these can be used for determination of sedimentation rates and places favorable for coal deposition. For example, in a depression along the southeastern boundary of the middle Amur zone there are a number of CTM in which volcanism underwent a complex evolution. Along the northwestern boundary of the zone there are a number of Cenozoic depressions where thickness and coal content of the deposits reaches a maximum. The same may be said of depressions of the Razdol'ninsk-Khankaish group. The presence of volcanic CTM "drives back" areas of terrigenous sedimentation to the margins of the CTM or beyond. Weakening or complete cessation of volcanic activity leads to an "onset" of sedimentation in areas occupied by domal CTM. This relationship was also established for older periods of tectonomagmatic activity [36]. Cenozoic morphostructures, including CTM, are best expressed in the present relief. Observation and study of these, along with other methods, can be of considerable help in estimation of coal resources, and in some cases, in correlation of sections in separate basins.

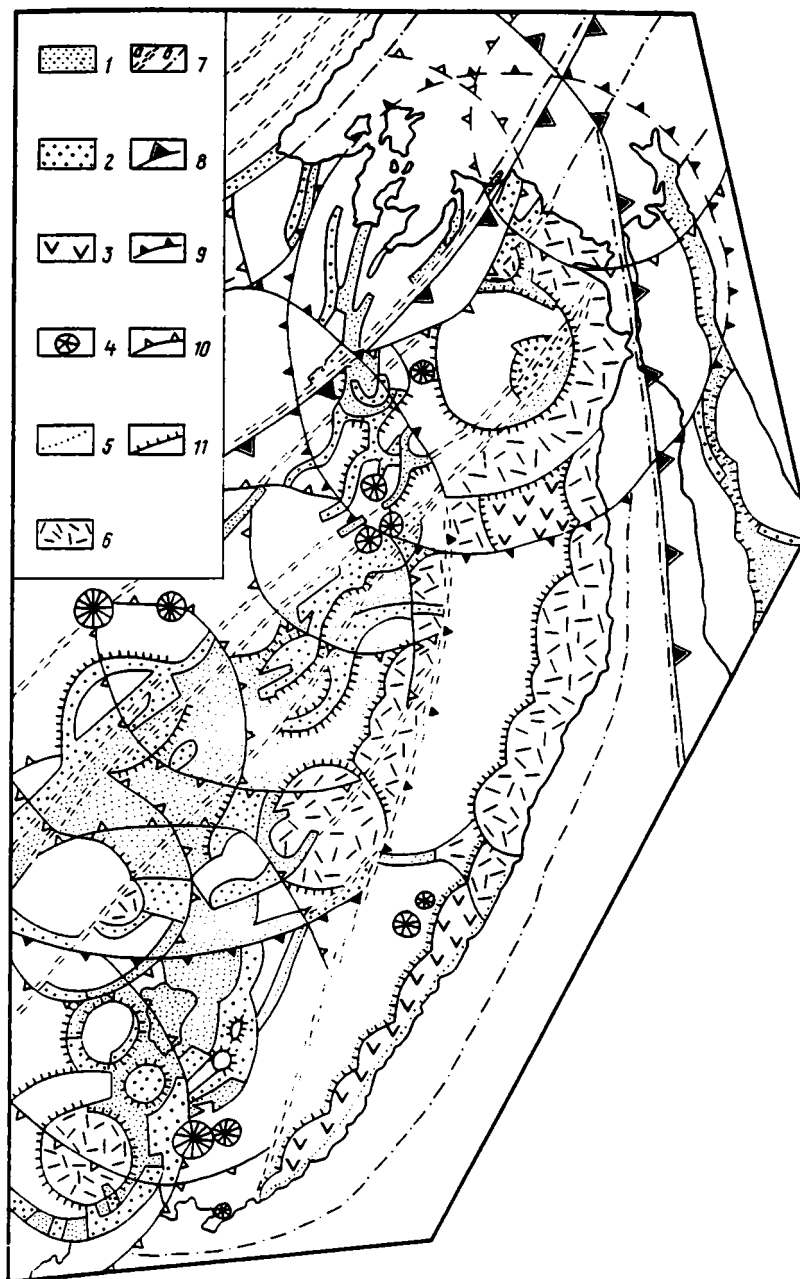


Fig. 1. Morphostructural position of Cenozoic depressions of the southern Far East. 1) Depression morphostructure filled with Cenozoic deposits; 2) same, showing disturbed zones; 3-6) volcanic zones: 3) mainly late Cretaceous; 4) individual centers; 5) active in Cenozoic; 6) late Cretaceous-Cenozoic; 7) zones of long-term faulting; 8-11) boundaries of morphostructures of various types: 8) highest; 9) first; 10) second; 11) lowest.

Analysis of the Cenozoic section in depressional morphostructures of the Khasan-Tugursk zone and volcanic structures of the west Sikhote-Alin (WSA) and East Sikhote-Alin (ESA) volcanic belts indicates the presence of a close association between the formation of terrigenous and volcanic sequences.

It has been shown [14-17, 19, 28, 32, 34-37, 41] that the sections are cyclic: relatively coarse grained terrigenous and volcanogenic sediments formed during initial subsidence predominate in the lower part; the middle part is of basic, intermediate, and mixed volcanites, which were deposited contemporaneously with terrigenous deposits, attesting to continued subsidence; and the upper part is typically acidic volcanites and terrigenous rocks, mostly coarser grained than the terrigenous material on the middle part. During deposition of the upper part of the cycle, the area of accumulation decreased in size to the point where hiatuses appeared in sedimentation and volcanic activity. The noted pattern of space-time association between volcanism, the composition of volcanic material, and terrigenous sedimentation can be used for correlation of events both within the volcanic belts and in the areas of formation of depressional morphostructures.

Most investigators involved with correlation of Cenozoic sequences in the Far East believe that discontinuities between cycles are related to tectonic quiescence and surface planation [14-17]. However, recent data [37] suggest that surface planation takes place mainly during extension and rift formation. This is a fundamental point to consider. Obviously, coal deposition coincides not with epochs of maximum discontinuity but with the initial or final stages of rifting.

Taking into consideration volcanism, Cenozoic deposits in the ESA and WSA volcanic belts, as well as the Khasan-Tugursk zone depressions, can be subdivided into four cycles: I) Paleocene-earliest Eocene; II) Eocene-Oligocene; III) Miocene; IV) Pliocene-Quaternary. All of the cycles are completely monotypic; any differences can be considered the result of cyclicity of a lower order. Each cycle can be subdivided into three parts: a) terrigenous and volcanogenic-terrigenous; b) volcanogenic (locally correlating with terrigenous rocks); and c) terrigenous or volcanogenic-terrigenous. Acidity of the volcanics increases upward through the section.

Rocks of cycle I unconformably overlie older rocks. They begin with a terrigenous and volcanogenic-terrigenous unit (Ia), with variable thickness; locally they are absent. The middle of the cycle (Ib) consists of basic and intermediate volcanites which are sometimes contemporaneous with terrigenous deposits of various grain sizes. The upper part of the cycle (Ic) is characterized by acidic, moderately acidic, and sometimes intermediate volcanites, in some cases accompanied by tuffogenic rocks. The upper part of the cycle generally overlies (unconformably the middle part). Rocks corresponding to this level occupy a smaller area or may be completely absent, which is expressed as an unconformity of irregular distribution. In the Khasan-Tugursk Cenozoic basins, cycle I is represented by an unconformity [32].

Cycle II is generally like the first in overall structure. The lower part (IIa), an essentially volcanogenic sequence, is thin or absent. Most of the cycle in the ESA and WSA volcanic belts is basic to intermediate volcanites (IIb). The cycle is completed with volcanogenic-terrigenous beds with lenses of basalt and andesite. Terrigenous rocks that fill depressions in the Khasan-Tugursk zone form a sedimentary cycle contemporaneous with the volcanogenic cycle II (volcanogenic-terrigenous cycle), as shown by volcanites of the Kuznetsov and Zaisanov suites, correlative with the lower part of cycle II. The makeup of the section in the sedimentary cycle indicates that locally it may be a closed type cycle.

In the ESA and WSA volcanic belts, cycle III begins with a volcanic-terrigenous unit (IIIa) or basis and intermediate volcanites (IIIb). The cycle ends with a sequence of terrigenous rocks of various grain sizes (IIIc) overlying an unconformity. In a number of places, the time of formation of the upper part of the cycle (IIIc) corresponds to a hiatus in sedimentation. The sedimentary cycle in the Khasan-Tugursk zone can be considered a closed type cycle, which is particularly well displayed in the Middle Amur group of basins. Sometimes the time of formation of the upper part of the cycle (IIIc) corresponds to a complete (Retikhovki basin) or partial (Khasan group of basins) unconformity.

In the volcanic belts cycle IV is composed of basalts and andesites with contemporaneous terrigenous rocks of various grain sizes, which locally change in time and space into terrigenous sequences. In the area of the Khasan-Tugursk zone, the make-up of cycle IV is

quite simple. At the base are coarse-grained rocks of the lower part of the Suifunsk suite (IVa), to which are added various amounts of basalt and andesite in the middle part (IVb). The upper part of the cycle (IVc), which corresponds to the beginning of the Quaternary, consists of terrigenous deposits. Rocks of this cycle are eroded, and in a few places they were apparently not deposited.

The cyclic nature of the section making up the Cenozoic volcanic-tectonic structures of the ESA and WSA volcanic belts and the closely related Khasan-Tugursk zone of basins suggests some overall patterns of development. Three parts have been noted in each cycle, corresponding to different environments of deposition. The lower part of the cycles (Ia, IIa, IIIa, and IVa), generally composed of terrigenous and volcanogenic-terrigenous rocks, indicates the initiation of subsidence. The main part of the coal beds apparently formed at this time. The middle part of the cycle (Ib, IIb, IIIb, and IVb) is characterized by increased rate of subsidence and intensity of volcanism. In several parts of the volcanic belt, active volcanism appeared essentially during the formation of the lower part of the cycle and then terrigenous units became thin or were totally absent. The first and second parts of the cycle thus represent the transgressive phase.

The composition of the upper parts of the cycles (Ic, IIc, IIIc, and IVc) attest to the inversion of tectonic movements. The presence of acidic and moderately acidic volcanites, coarser grained contemporaneous terrigenous rocks, and partial unconformities or complete absence of beds suggests a general bulging up of the area. The upper part of the cycles thus correspond to the regressive phase and are absent where unconformities are present.

The distribution of cyclicity in space and time shows that the volcanic belts began to subside earlier than the Khasan-Tugursk zone. For example, cycle I is characteristic for the ESA and WSA volcanic belts, while the Khasan-Tugursk zone was not subsiding and was undergoing erosion at this time. At the time of formation of cycle II subsidence of the area was taking place, adjacent to the volcanic belts. This period correlates with the thickest (350 to 1100 m) sedimentary cycles and a wide area of occurrence of the deposits. The subsidence did not involve only the Khankaish massif. The period of cycle II is characterized by maximum extent of the area of subsidence, but the thickness of the sediments is somewhat less (150-700 m). Thereupon, there was some restriction of the area occupied by rocks of the volcanic cycle III. Finally, maximum extent of sedimentational area is noted on formation of cycle IV, which nearly everywhere is volcanogenic-sedimentary, with a decrease in thickness (20-200 m).

Obviously, an increase in volcanic activity leads to an increase in downward tectonic movement and to involvement of areas around the volcanic belts, where the volcanic-sedimentary (transitional) and sedimentary cycles are formed. Both the zone of terrigenous sedimentation and the zone of volcanic activity grew wider from cycle to cycle as a result of subsidence of areas away from the axial parts of the structures. For the Khasan-Tugursk zone this is expressed in "rolling" of waves of sedimentation and volcanism from east to west, which is especially typical of the Khankaish and Khasan groups of basins. The volcanites of cycle I are thus essentially not present outside of the volcanic belts. At the time of formation of cycle II volcanic activity was present even in depressions adjacent to the volcanic belts. During cycle III and especially IV, volcanic activity has expanded throughout the entire Khasan-Tugursk zone and locally beyond. This overall pattern can be used for correlation of sections in different basins. We will consider several debatable correlations.

The Novopos'et suite (latest Paleocene-earliest Eocene) in the Khasan zone is composed of acidic and moderately acidic volcanites (absolute age 41-42 million years). This suite, according to the Third Far Eastern Stratigraphic Commission [32], is placed in the lower part of cycle II. However, the acidic and moderately acidic volcanites suggest that it may correspond to the regressive phase of cycle I, rather than the transgressive phase of cycle II. In this connection, part of the Nazimov suite, contemporaneous with Novopos'et volcanites, should be included in the upper part of cycle I (Ib). Between cycles I and II, then, there may be a brief hiatus here, corresponding to the beginning of the Eocene. From this it follows that the lower parts of the section in the Uglov, Arsen'ev, Bikin, and Evoron-Chukchagirsk groups of basins may be somewhat younger.

According to the statement of the stratigraphic scheme [32], the sequence of acidic and moderately acidic effusives in the Khasan zone are contemporaneous with the clayey-tuf-

fite sequence. However, the grain size of the terrigenous beds suggests that they belong to the transgressive part of a given cycle, while the sequence of effusives should be referred to the regressive phase of the cycle. The contemporaneity of these two sequences can thus be considered doubtful.

The placement of the lower part of the Pavlovki suite (Khankaïsk massif) in the upper Oligocene provokes serious doubt. Cycle III (lower to middle Miocene) everywhere unconformably overlies cycle II (Oligocene). This unconformity has been traced as far as the Zeïsko-Bureïnsk and Ushumunsk groups of basins. The composition of the lower part of the Pavlovki suite suggests deposition in a transgressive environment. Considering this, it may be proposed that the beginning of cycle III, which includes the Pavlovki suite, be referred to the early Miocene, since the unconformity between cycles II and III occurs at the latest Oligocene-earliest Miocene.

If it is the official point of view that subsidence of the Khankaïsk massif area occurred at the end of the Oligocene [32], then subsidence began here when upward tectonic movements prevailed everywhere else.

It has been shown above that alternate subsidence and expansion of the area of sedimentation took place in early Miocene, while at the end of late Oligocene and in earliest Miocene upward movements were characteristic.

The Sandugansk suite, composed of basic volcanites, are placed in the upper part of cycle III, and beds at the top of the unit are considered younger than volcanites of the Kizinsk suite (lower to middle Miocene). There is reason to suppose that the Sandugansk basalts are characteristic of the transgressive phases of the cycles. In the stratigraphic scheme, they are placed partly at the level of the regressive phase of cycle III (lower upper Miocene).

Although the views relative to the Novopos'et suite, acidic effusives, the lower part of the Pavlovki suite, and the Sandugansk basalts are expressed as an hypothesis, they do not contradict the concept of the cyclic nature of the section of both volcanic and terrigenous Cenozoic deposits. And what is more, they are also supported by an analysis of cyclicity of higher orders, which are not examined here. The close association between magmatic domal morphostructures and depressional morphostructures is beyond doubt. Their formation was under endogenic regimes progressing in a certain sequence and having the same general trend. Because of the appearance of the appearance of cyclicity simultaneously with Cenozoic depressions filled with terrigenous rocks and volcanic belts, divergence from the standard scheme is local in nature and should not contradict the overall trend. Therefore the more precise stratigraphic correlations proposed here for certain suites and sequences (or parts there of) on the basis of paleofloral studies are in accord with the morphostructural setting.

LITERATURE CITED

1. A. G. Ablaev, Upper Cretaceous Flora of Eastern Sikhote-Alin and Its Significance for Stratigraphy [in Russian], Nauka, Novosibirsk (1974).
2. A. G. Ablaev, Geology and Evolution of the Flora along the Coast of the Sea of Japan (in Late Cretaceous and Tertiary Time) [in Russian], Nauka, Moscow (1978).
3. A. G. Ablaev, Neogene Coal Deposition in the Sikhote-Alin Area: Current Problems in Paleontology and Biostratigraphy in the Development of Mineral Resources [in Russian], Izd-vo VPO, abst. of XXVI Session, Sverdlovsk (1980), pp. 3-4.
4. A. G. Ablaev and V. P. Solomonovskaya, Stratigraphy of Flora-bearing Beds of the Khasan Region of Southwestern Primor'e: Paleobotany and Stratigraphy of Continental Deposits of the Soviet Far East [in Russian], Izd-vo DVNTs, Akad. Nauk SSSR, Vladivostok (1975), pp. 5-15.
5. M. A. Akhmet'ev, Climatic Fluctuations During the Paleogene and Neogene in the Middle and High Latitudes of the Globe (Based on Paleobotanical Data). Paleontology. Marine Geology. (22nd International Geological Congress, Dokl. Sov. Geol.), Nauka, Moscow (1976), pp. 138-146.
6. M. A. Akhmet'ev, Results of the Third Far Eastern Interdepartmental Stratigraphic Symposium (Section on the Paleogene and Neogene): Stratigraphy and Flora of the Neogene of the Far East [in Russian], Nauka, Moscow (1979), p. 5-7.

7. M. A. Akhmet'ev, G. M. Bratseva, and R. S. Klimova, "Temporal correlatives in Primor'e of the Engelhardia bed of Korea," Dokl. Akad. Nauk SSSR, 209, No. 1, 167-170 (1973).
8. M. A. Akhmet'ev, G. M. Bratseva, V. N. Sinel'nikova, and A. I. Chelebaeva, "Climatic optimum in the Neogene of Kamchatka," Izd-vo Akad. Nauk SSSR, Ser. Geol., No. 8, 70-78 (1984).
9. T. N. Baikovskaya, Upper Miocene Flora of Southern Primor'e [in Russian], Nauka, Leningrad (1974).
10. L. A. Baskakova and N. S. Gromova, "Phytostratigraphic differentiation of Paleogene deposits of Southwestern Primor'e," Sov. Geol., No. 11, 68-78 (1982).
11. O. A. Betekhtina, Biostratigraphy and Paleogeography of the Carboniferous and Lower Permian of Angaraland According to Nonmarine Bivalves [in Russian], Ph. D. Diss., Sib. Otd. Akad. Nauk SSSR, Novosibirsk (1978).
12. S. F. Biské, "Paleogene climate of northeastern Siberia," Geol. Geofiz., No. 1, 20-27 (1981).
13. M. D. Bolotnikov, Spore and Pollen Assemblages in the Tertiary Deposits of the Western Coast of the Sea of Japan [in Russian], Nauka, Moscow (1979).
14. V. G. Varnavskii, Paleogene and Neogene Deposits of the Middle Amur Basin [in Russian], Nauka, Moscow (1971).
15. V. G. Varnavskii, Geology and Mineral Resources of the Cenozoic Sedimentary Basins of the Southern Mainland of the Far East [in Russian], Ph. D. Diss., Inst. Tektonika i Geofiz., Khabarovsk (1981).
16. V. G. Varnavskii, Patterns of Change in Coal Content of Cenozoic Intracontinental Sedimentary Basins (as in the Amur Area and Primor'e) [in Russian], abst. 27th session Internat. Geol. Cong., Tom 9, No. 2, Nauka, Moscow (1984), pp. 321-322.
17. G. M. Vlasov, "Cyclicality of volcanic processes," in: Volcanism and the Geochemistry of its Products [in Russian], Nauka, Moscow (1967).
18. Volcanic Belts of Eastern Asia. Geology and Metallogeny [in Russian], A. D. Shcheklova (ed.) Nauka, Moscow (1984).
19. Geology of the USSR. Primor'e Region, Tom 32, No. 1 [in Russian], Nedra, Moscow (1969).
20. A. V. Gol'bert, Climate of the Jurassic, Cretaceous, and Paleogene of Siberia and its Role in Lithogenesis [in Russian], abst. 27th Session Internat. Geol. Congress, Tom 2, Nauka, Moscow (1984), pp. 63-64.
21. Yu. Ya. Gromov and N. S. Gromova, "Some patterns of change in the coal-bearing section of Paleogene and Neogene deposits on the western slopes of Sikhote-Alin," in: Coal-Bearing Formations in Selected Regions of the USSR [in Russian], Izd-vo Akad. Nauk SSSR, Moscow-Leningrad (1961), pp. 487-495.
22. O. V. Zhukov, Patterns of Spatial Change in Superficial Deposits of the Urals [in Russian], abst. 27th Internat. Geol. Cong., Tom 9, No. 2, Nauka, Moscow (1984).
23. M. M. Koshman, "Tertiary flora of the Bikin brown coal deposit," Botan. Zh., No. 2, 265-271 (1964).
24. V. V. Krapiventseva, Coals of the Middle Amur and Bikin Basins [in Russian], Nauka, Moscow (1972).
25. A. N. Krishtofovich, "Tertiary flora of Pos'et Bay, collected by E. E. Ahnert in 1919," Materiali po Geol. i Polezn. Iskop. Dal. Bost., No. 11, 1-28 (1921).
26. N. M. Maksimov, Problems in Global, Regional, and Local Tectogenesis in Coal Geology [in Russian], abst. 27th Internat. Geol. Cong., Tom. 9, No. 2, Nauka, Moscow (1984).
27. K. V. Mironov, Geologic Basis for Coal Exploration [in Russian] Nedra, Moscow (1973).
28. A. V. Oleinikov, Evolution of Cenozoic Volcanism of Primor'e, in: Geodynamic of Volcanism and Hydrothermal Processes [in Russian, Obl. Izd-vo, Petropavlovsk-Kamchatka (1974), p. 79.
29. V. I. Podolyan, Patterns of Variation in Coal Basins and Deposits of the Pacific Mobile Belt in the USSR [in Russian], abst. 27th Internat. Geol. Cong., Tom. 9, No. 2, Nauka, Moscow (1984), pp. 313-314.
30. S. M. Popova, Cenozoic Continental Malacofauna of Southern Siberia and Adjacent Areas [in Russian], Nauka, Moscow (1981).
31. Practical Stratigraphy. Development of a Stratigraphic Base for Large-Scale Geological Surveys [in Russian], Nedra, Leningrad (1984).
32. Resolutions of the Third Interdepartmental Regional Stratigraphic Symposium on the Precambrian and Phanerozoic of the Far East. Vladivostok, 1978 (Explan. List and Stratigr. scheme) [in Russian], Izd-vo MSK SSSR, Magadan (1982).

33. E. M. Rudich, Basic Patterns in the Tectonic Evolution of the Primor'e, Sakhalin, and Japan as Zones of Transition from Continent to Ocean [in Russian], Izd-vo Akad. Nauk SSSR, Moscow (1962).
34. V. I. Rybalko, "Stages in the development of orogenic volcanic belts," in: Geodynamics of Volcanism and Hydrothermal Processes [in Russian], Obl. izd-vo, Petropavlovsk-Kamchatka (1974), pp. 61-62.
35. S. M. Tashchi, "Paleomorphological reconstruction in areas of orogenic volcanism," in: Geomorphostructure of the Far East [in Russian], Izd-vo DVNTs, Akad. Nauk SSSR, Vladivostok (1978), pp. 43-55.
36. S. M. Tashchi, Permian Geologic-Geomorphologic Systems of Primor'e, in: Morphostructures and Paleogeography [in Russian], Izd-vo DVNTs, Akad. Nauk SSSR, Vladivostok (1979), pp. 16-30.
37. S. M. Tashchi, "Connection between rift morphostructures and morphostructures of the central type," in: Morphostructural Studies of the Far East [in Russian], Izd-vo DVNTs, Akad. Nauk SSSR, Vladivostok (1983), pp. 23-40.
38. Sh. G. Ul'myasbaev, "New information on the tectonic structure of the Lower Bikin brown coal deposits," in: II Far Eastern Geological Conference of Geologist-Colliers. Artem, Primor'e Region [in Russian], NTO (Mining) (1974), pp. 14-16.
39. Yu. B. Ustinovskii, Khan Don Sik, M. D. Bolotnikova, et al., "Stratigraphy and environment of deposition of Cenozoic deposits," in: Geology of Northeastern Korea and Southern Primor'e [in Russian], Nauka, Moscow (1966), pp. 162-261.
40. L. I. Fot'yanova, "Upper Eocene pre-Turgaisk flora of Ancient Beringia," Botan. Zh., No. 4, pp. 425-436 (1984).
41. G. I. Khudyakov, E. P. Denisov, A. M. Korotkii, et al., "Southern Far East," in: History of Development of Relief in Siberia and the Far East [in Russian], Nauka, Moscow (1972).
42. L. Hably, "Climatic changes in the area of central Paratethys during the Tertiary (based on the macroflora)," Stud. Botan. Hung., 13, 39-46 (1979).
43. K. Huzioka, "The Tertiary floras of Korea," J. Min. Col. Akita Univ., Ser. A, 5, No. 1, 1-83 (1972).
44. S. Oishi, "On the genus Engelhardia and its occurrence in the Paleogene of Korea," J. Geol. Soc. Jpn., 43, No. 508, pp. 56-59 (1936).
45. N. J. Shackleton and J. P. Kennett, Later Cenozoic Oxygen and Carbon Isotopic Exchange at DSDP (Deep-Sea Drilling Project), Site 284: Implications for Glacial History of the Northern Hemisphere and Antarctica, Initial Repts. DSDP, Washington, D.C., 29, 801-807 (1975).
46. T. Tanai and K. Huzioka, "Climatic implications of Tertiary floras in Japan," in: Tertiary Correlation and Climatic Changes in the Pacific, the Pacific Sci. Cong., Symp. No. 25, Tokyo (1967), pp. 89-94.
47. T. Tanai and K. Uemura, "Engelhardia fruits from the Tertiary of Japan," J. Fac. Sci. Hokk. Univ., Ser. 4, 20, No. 2-3, 249-260 (1983).
48. C. Wahrhaftig, J. A. Wolfe, E. B. Leopold, and M. A. Lanphere, The Coal-Bearing Group in the Nenana Coal Field, Alaska, U. S. Geological Survey Bull. 1274-D (1969).
49. J. A. Wolfe and D. M. Hopkins, Climatic Changes Recorded by Tertiary Land Floras in Northwestern North America, in: Tertiary Correlations and Climatic Changes in the Pacific. The 11th Pacific Sci. Cong., Symposium No. 25, Tokyo (1967), pp. 67-76.

CATAGENESIS, METAGENESIS, AND METAMORPHISMS IN ROCK FORMATION BASINS OF MIOGEOSYNCLINES

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The paper discusses various ways of reconstructing rock formation processes in miogeosynclinal basins complicated by folding. The methods recommended are based on analysis of the original features of sedimentogenesis which determined the course of postsedimentary change. The important problem of relationships between catagenesis on the one hand and metagenesis and metamorphism on the other is discussed. The theoretical principles are illustrated by recent data from studies of lithology in the Verkhoyan complex and data from numerous publications.

Genetic studies are the leading aspect of modern lithologic research [26]. Postsedimentary alterations of sedimentary rocks should also be studied on a genetic basis. Actual descriptions are insufficient for understanding the processes responsible for alterations and inaccessible to direct observations; different methodological principles are needed. Rock formation basins in tectonically mobile miogeosynclinal regions transformed into folded areas are particularly complex entities, and special methods are required for deciphering them.

The investigator is faced with a variety of problems, such as the influence of exogenous (facies-landscape) conditions of sedimentogenesis and endogenous factors in lithogenesis diagenesis and subsequent rock alterations), interrelationships of sedimentary rock catagenesis, and metamorphism of these rocks, etc. The first of these problems and possible solutions have been discussed in [35] with special reference to the lithology of the Verkhoyan folded miogeosynclinal complex of Mesozooids of the northeastern USSR. We will describe it briefly and then concentrate attention on reconstructions of catagenesis and postcatagenetic lithogenesis. So far, no one has succeeded in deciphering unequivocally those processes affected by a large number of factors. Their mechanisms can be explained on the basis of recent theoretical studies in geomineralogy [11, 12, 31, etc.] and hydrochemistry of lithogenesis [13, 27, 28, etc.]; these studies are performed on a genetic basis using data from a preliminary detailed lithologic-facies and formational analysis of the objects studied [24-26]. The data from stadial analysis of postsedimentary neomorphs at the various levels of organization of matter (mineral, facies, and formation) and historic-geologic descriptions of the development of lithogenetic zonalities during the rock basin evolution prior to folding should be combined in order to understand the history of complex dislocated bodies [34].

Outline of Sedimentogenesis and Lithogenesis Environments in the Verkhoyan Complex (Primary Data)

The Verkhoyan complex of Late Paleozoic, Triassic, Jurassic, and Early Cretaceous rocks forms a thick (>20 km) lens of dislocated terrigenous rocks, largely contained between the right banks of the Lena, Aldan, and Yana rivers. In turn, it can be divided into three facies subcomplexes, each associated with a distinctive paleotectonic structure (or a portion of such a structure) and represents a particular stage in geotectonic evolution, i.e., corresponds to a genetically determined body — a formation [25]. The following formations are distinguished: Late Paleozoic valley-fan alluvial cone formation of the slope of the sea basin of the Paleoverkhoyan miogeosynclinal trough (F-1); the Early Mesozoic moderate-deep rocks of margin-continental basin of the Paleoverkhoyan-Indigirka trough (F-2); and Late Jurassic-Early Cretaceous coal-bearing alluvial-deltaic formation of the Upper Verkhoyan trough (F-3). Each of these formations consists of two transgressive-regressive macrocycles of regular alternating facies or two subformations. According to the variable quantitative ratios of the facies, each subformation is divided into gradations in the lateral direction. A study of their struc-

ture and proportions [34, 35] has shown that during sediment accumulation periods in F-1 and F-2, the near-platform (western and southwestern) margins of the miogeosynclinal paleostructure were areas with a predominant facies of river discharges into sea or open mobile shoals; the northeastern gradations are seafloor sediments from areas situated farther offshore: turbidites, submarine slump accumulations, sand grain flows, and high-Corg and high-pyrite silt-pelite from margins of alluvial cones and depressions. The regular succession of regressions and transgressions shifted the boundaries of these facies eastward and westward, but the general proportions remained unchanged until the Middle Jurassic. The sea basin of a bowl type was filled at an avalanche rate (from 24 to 240 mm per 1000 years, according to [1], with material brought into foredeltas and redistributed material in the depth of the basin by auto-kinetic flows, which formed the systems of valley-fan cones in shallow or moderate-deep environments (not deeper than 0.5-1.5 km). Most terrigenous material was supplied by two large rivers from southeastern and northwestern margins of the Siberian platform and from mountains that arose periodically in the territory of current Stanovoi and Aldan mountain ranges, Dzhugdzhur, Sette-Daban, and parts of South Taimyr; these were the main sources of terrigenous material rather than internal rises or cordilleras (although isolated islands could arise sometimes at the end of the Permian and the Early Triassic and Jurassic). During the Jurassic this sedimentation basin began to be divided into separate basins in the course of the Late Mesozoic regeneration of the earth's crust in the northeastern Asia [17]. Deep thermal activation that began earlier in the Triassic was intensified at the boundary of the sedimentary cover and consolidated crust, where anatectic magma [20] appeared and in small portions began to intrude through the faults; the process continued up to the Cenozoic. During the Late Jurassic and Early Cretaceous the marginal basins - Verkhoyan and Lena-Anabar - became separated; Lazurkin (1948) and Vinogradov (1970) have proved that these basins were not compensational depressions in front of the folded Verkhoyan meganticlinorium, because the latter became an elevation much later than the Mesozoic folding was completed [34].

The long evolution of this giant rock formation basin with periods of subsidence and tectonic restructuring produced a complex zonality of deep catagenetic alterations, intensified locally by early metamorphic change. The zonality was discovered back in the 1950s in Western Verkhoyan [10]; it has been confirmed by our studies for the entire region and described in detail. Despite the rapid sinking of sediments in a miogeosynclinal environment, the specifics of the alterations of genetic types of sediments were not fully homogenized [35]. The stages of lithogenesis are best documented by indicator minerals and textures of sandstones formed from sandy sediments of the following facies that were sorted well and washed of the clay fraction: 1) grain flows near slopes of sea basin depressions; 2) formations of mobile sea shoals (sand bars, spits, etc.); and 3) deltaic cones and river valley alluvia. Since these facies appear in virtually all gradations of miogeosynclinal and neighboring marginal-platformal formations, they are convenient for correlations of the general regional lithogenetic zonality.* Nine zones of progressive alterations have thus been identified: I) slightly altered clay matter and intact sedimentogenic textures (the substage of weak initial catagenesis); II) mainly chloritic film and silicic pore cement and initial fragment regeneration (moderate catagenesis); III) mainly chloritic-quartzose film-pore cement and frequent conformal structures (massive development of gravitational corrosion texture as a feature of the early substage of deep catagenesis or late catagenesis); IV) quartzose cement of the "welded" type, frequent conformal and rare incorporational textures; V) mainly conformal-incorporational textures with regenerational quartz and feldspathic cement; VI) blastic textures on conformal-incorporational contacts of quartz fragments (initial metagenesis); VII) differential slide textures, spike-shaped neomorphs of a sericitelike hydromica, quartz, or albite (metagenesis and early metamorphism; VIII) massive blastic spikelike textures and segregational structures, with metamorphogenic muscovite, quartz, and albite; and IX) metamorphogenic biotite in metasandstone and quartzose-micaceous blastopsammitic schist (metamorphism, mainly of greenschist stage). Miogeosynclinal formations are characterized mainly by features of zones V-VII or later and, less frequently (in the formation F-3), zones II and IV. Products of earlier lithogenesis can be found as relicts, since within each such zone alterations of rocks of different types are anisotropic. For example, calcareous sandstones (with basal or pore calcitic cement of early generation) remained virtually unchanged and now have the same appearance in all of these zones. Their sedimentogenic texture remained, as it were, sealed by a carbonate filler; its mosaic-granoblastic texture is evidence of its postsedimentary origin (Fig. 1a, b). Calcite slightly corroded fragment particles and prevented their further alteration (regeneration,

*The other rocks studied in this complex are not described in this paper.

quartzification, albitization, etc.), except only for a partial chloritization of terrigenous biotite and hydromicatization of certain plagioclases, probably begun before calcite crystallization. With a drop in the amount of carbonate matter, even within a bed, incorporational intrusions of grains into other grains outgrowths of authigenic quartz, albite, sericite, and other minerals appeared immediately. This shows that calcite was crystallized in pores that were open and caused the rock to solidify even before the development of deep-catagenetic mineral parageneses. Sandstones of this type are usually found at a contact with variably thick members of silt-clay rocks; more often it is found in thin interlayers in such members. Their formation can be explained by degassing of CO₂-saturated fluids expressed from clays, i.e., by elisional processes [28]. However, these entities play a subordinate role in the Verkhoyan complex.

In the widespread carbonate-free sandstones (especially in the thick members of these rocks) the postsedimentary change has been affected not only by structural-textural features of the original sediment, but also by clastogenic components (see Fig. 1c, d). This is clearly seen in comparisons of sandstones from different formations. For example, in formations F-1 and F-2 graywackes are predominant (quartzose-feldspathic, feldspathic-quartzose, and quartzose); graywacke arkoses are less frequent (mainly in F-2); finally, mesomictic quartzose sandstones are found only at selected stratigraphic levels of the Carboniferous, the Middle and Upper Triassic, and the Lower Jurassic, at the bottom of selected transgressive sedimentary mesocycles. In transitions across the course of tectonic structures toward marginal-plat-formal formations, these sandstones are replaced by members of oligomictic silica-clastic quartzose rocks (terminology of Shutov [30]). Most of these varieties contain quartz-chlorite-hydromica neomorph aggregates (Fig. 2). The quantitative correlations of the above minerals and their typomorphic features vary from one case to another, depending on the proportions of terrigenous quartz and lithoclasts and the composition of these lithoclasts. Different (qualitatively new) sets of authigenic minerals appear in settings where the combination of rock-forming components has changed substantially, as, for example, in the sandstones of the Lower Carboniferous of F-3 in the Verkhoyan trough, classified as a peculiar group of "neutral arkoses" (term suggested by Kossowskaya) (see Fig. 1a, c). By the time of their accumulation, the provenance areas of the sedimentary basin had been redistributed by the end of the miogeosynclinal stage. F-3 sediments were mainly produced as a result of erosion of Precambrian diaphthorites and Early Mesozoic granodiorites and tonalites of the Aldan-Stanovoi region [10, 34]; their terrigenous components consist mainly of plagioclases of the oligoclase-andesine series, less frequently of potash-feldspar and quartz, with a considerable admixture of biotite, muscovite, and a large amount of accessory femic minerals. Similar parageneses have been described [41, 42, etc.] in rocks of Late Cretaceous basins of British Columbia (Vancouver and the Gulf Islands) and Paleocene and Eocene basins of California (Western Olympia and Santa Ynez Mountains) adjacent to older granodiorite massifs. Typical authigenic minerals in the cement of such sandstones are zeolite (mainly laumontite) in a paragenesis with corrensite and sphene. The main sources of matter from which they were formed were probably terrigenous minerals which contained calcium (neutral plagioclase, epidote, hornblende, and garnet; for corrensite and sphene, biotite, etc.). This is supported by stadiol analyses - in particular, observations of laumontite pseudomorphoses after the above minerals in sandstone polished sections with typomorphic features of the early deep catagenesis. Prior to the metagenesis stage (zone V), laumontite was replaced by epidote and calcite of a late generation; at the same time, the relative content of authigenic quartz and (due to plagioclase) albite was increased. Laumontite (or its substitution products) is concentrated amid the rocks of the F-3 formation only in sandstones from the facies of deltaic subaerial cones and riverbed alluvia of a large river (see Fig. 1a, c); probably this happened because the slightly reductive and neutral or alkaline environment conducive to zeolite genesis was inherited during catagenetic processes from a similar chemical surroundings of interstitial solutions in bottom facies sediments.

In an indirect way, through the petrographic pool of formations, postsedimentary mineral development was affected collectively by a variety of sedimentogenetic factors. First of all, it was the syndimentary tectonic regime which determined the location, size, topography, and, eventually, the composition of the substrate that was eroded and the facies and climatic sedimentation settings. Indications of the latter's influence on rock formation in miogeosynclinal basins are more disguised, but they can also be deciphered. We mentioned earlier the levels at which quartz-saturated sandstones appear at the bottom of selected transgressive sedimentary cycles in the Verkhoyan complex. For the most part, they coincide in time with periods where, according to paleofloristic and general geologic data, humid and hot climates prevailed. The intensification of chemical weathering in such periods certainly favored the

development of mineralogically mature terrigenous material. The frequent periodic activations of tectonic motions and the associated intensive rates of erosion, however, prevented the completion of maturation of material in sediments. Even so, at the end of some of the regressive periods of sedimentation, during temporary lulls in tectonic activity, the alimentation provinces could develop crusts of weathering; subsequent erosion of these crusts gave rise to specific terrigenous mineral parageneses, termed aposaprogenic by Shutov [31]. In developing Shutov's theory, we can note that the peculiarity of these parageneses in the rocks of miogeosynclinal formations was not completely lost even after the end of deep cata- and metagenesis stages. Sandstones with aposaprogenic paragenesis in zones VI-VII exhibit a strong presence in the cement of regeneration quartz (or two and more generations), intensive quartzification of feldspar fragments, and widespread terrigenous grains of recrystallization structures of recrystallizational-granulational blasts on contacts of terrigenous grains (see Fig. 2a). All the other, more polymictic sandstones contain metagenetic alterations of a different type: intergrain granolepidoblastic quartzose-chloritic-micaceous aggregates, which prevented the broader development of regeneration cements and recrystallization-blastitic textures, instead of which, "spike-like" or "bearded" textures of mica ingrowths in strongly corroded edges of terrigenous grains are common in these rocks (see Fig. 2b).

Repetitions of similar paragenetic mineral associations in sections provide a basis for regional correlations of postsedimentary change of rocks of different compositions at the formation and subformation scale; the conclusions presented below were drawn on this basis.

The intensity of the ultimate change of rock in the folded region that replaced the miogeosyncline was determined by thermal activation of the earth's interior and tectonic displacement more than by the depth of subsidence of these rocks in the basin before folding. The deepest postcatagenetic alteration in the Verkhoian complex occurred mainly along tectonically weakened portions, where deep diagonal faults cross local gravitational field minima, i.e., over the probable foci of Late Mesozoic granitization of the basement in this basin [36, 37]. In plan, the metamorphism zones exhibiting spotty contours and cross stratigraphic boundaries; the most advanced alterations of zone IX with metamorphogenic biotite, staurolite, and garnet are found not only in the oldest Carboniferous rocks but also in the Lower and Upper Permian, and sometimes even in the Middle Triassic (on the Altan and Bukhuruk rivers). Their position in the modern structures do not correlate with fluctuations of the thickness of overlying beds (Fig. 3). Besides these areas, there are much more extensive territories where Carboniferous and Permian rocks at the very bottom of the Verkhoian complex were not metamorphosed: their alterations increase down the section very gradually and remain within zones VI-VII (for example, in the axial portion of the Kuranakh anticlinorium, on the Dyanyshka River, and in the Kharaulakh anticlinorium at the lower reaches of the Lena). This is evidence of a superimposed nature of metamorphic alteration; these are formations of thermal domes associated with areas of intensive fissuring of rocks near faults with an outer thrust component, i.e., tectonic structures favorable for fluid migration, which was the major factor of heat transfer.

In miogeosynclinal tectonic conditions rock formation basins were thus exposed to two basic mechanisms of lithogenetic alteration: one resulted in a buildup of structural and mineralogic change in rocks as they subsided and were subjected to increasing lithostatic pressures and temperatures; the other mechanism produced locally superimposed alterations of a dynamic-thermal nature during tectonic activations and dislocations. The two mechanisms were interrelated in space and apparently genetically, operating as components of a common fluid-rock system that passed through a continuous-intermittent evolution. We explain this process below.

Reconstruction of the Mechanism of Postsedimentary Processes of Various Types in Miogeosynclinal Environments

Lithogenetic alterations caused by rock subsidence are disguised by metagenetic alterations superimposed upon them in the folded region. Even so, some of the features of initial elisional catagenesis (according to the Kholodov's definition [27]) have survived. Essentially, the active force that determines the gas and water composition during catagenesis in this case is exerted by clay strata. As these strata sink rapidly, the physicochemical processes that evolve result in an accumulation of gas-water fluids. Fluids are expressed from clays into sand rock beds, leading to authigenic mineral formation. Migration of $\text{CO}_2\text{-H}_2\text{S}$ waters to a depth of 2 km, for example, is conducive to crystallization of early catagenetic calcite in intergrain spacings. At a depth of 3-4 km an important role is played by dehydration-caused montmorillonite-to-mica alteration, and the influx into collector beds of substan-

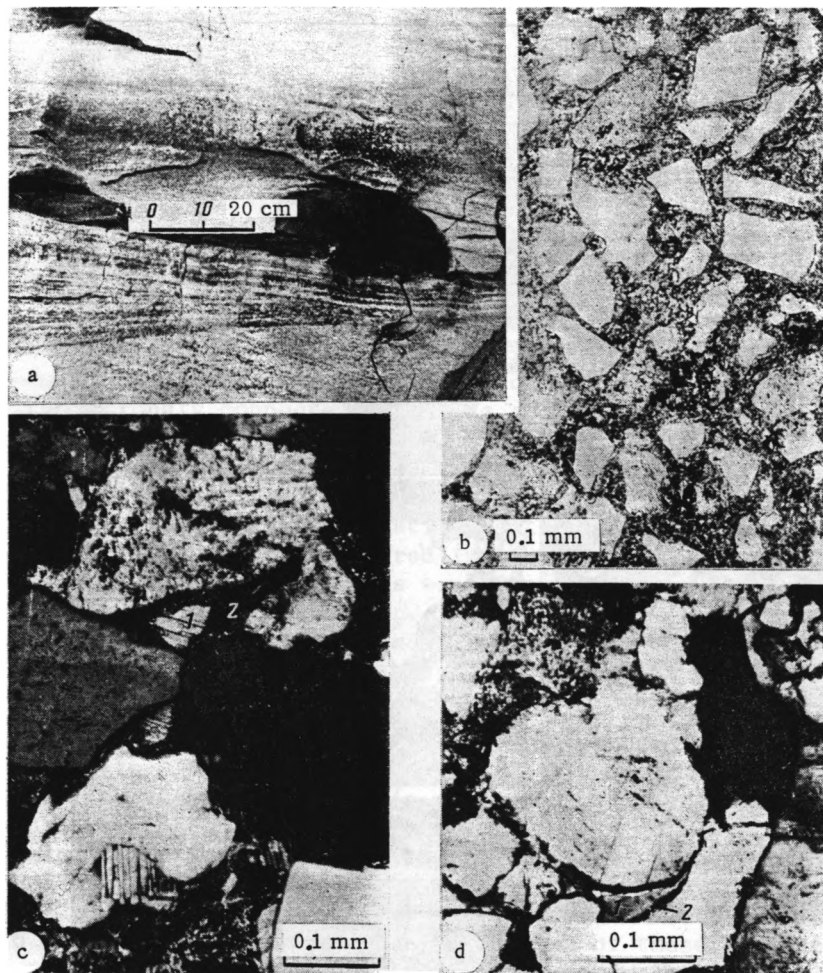


Fig. 1. Varieties of sand rock cement in zone III of the beginning of early deep catagenesis, Late Mesozoic formation F-3, Verkhoyan trough; photographs of outcrops (a) and polished sections without analyzer (b) and with crossed nicols (c, d): a) calcareous nodules (dark) in a member of obliquely stratified sandstone with corrensite-zeolite cement (facies of sand sediment in the bed of a large river; Dzhardzhan suite, Aptian stage; Menkere River); b) calcite intergranular filler of an early catagenetic nodule (see Fig. 1a) protecting clastic particles from regeneration; c) outside the nodule laumontitic pore cement (1) and corrensitic film cement (2) rim, partly regenerated plagioclase, and quartz fragments; d) quartzose pore cement (1) and chloritic film cement (2) in quartzose mesomictic sandstone (facies of silt-sand sediments of the near-bed flood valley area in Kyusyur coal-bearing suite, Hauterivian stage, left bank of the Lena River near Kyusyur Village).

ces dissolved in water, especially the excess SiO_2 precipitated from chlorite formations. The crystallization of SiO_2 could produce mosaic-regeneration textures observed in sandstones of zones II-V, which for some reason were not carbonitized during earlier catagenesis. Detailed mechanisms of these and related processes have been investigated in [27, 28]. We should add that the processes must be affected by the structural features of miogeosynclinal formations and especially proportions of clay and silt-sand sediments and their original compositions. These variations may be responsible for the peculiarities of catagenesis in Verkhoyan formations; they have a much higher sand content than the substantially clayey formations of eastern Ciscaucasia, used by Kholodov to illustrate typomorphic features of elisional processes. In a typical elisional catagenesis, sandy rocks play a relatively passive role, whereas in the Verkhoyan complex only a small proportion of sandstones remain passive (sandstones from

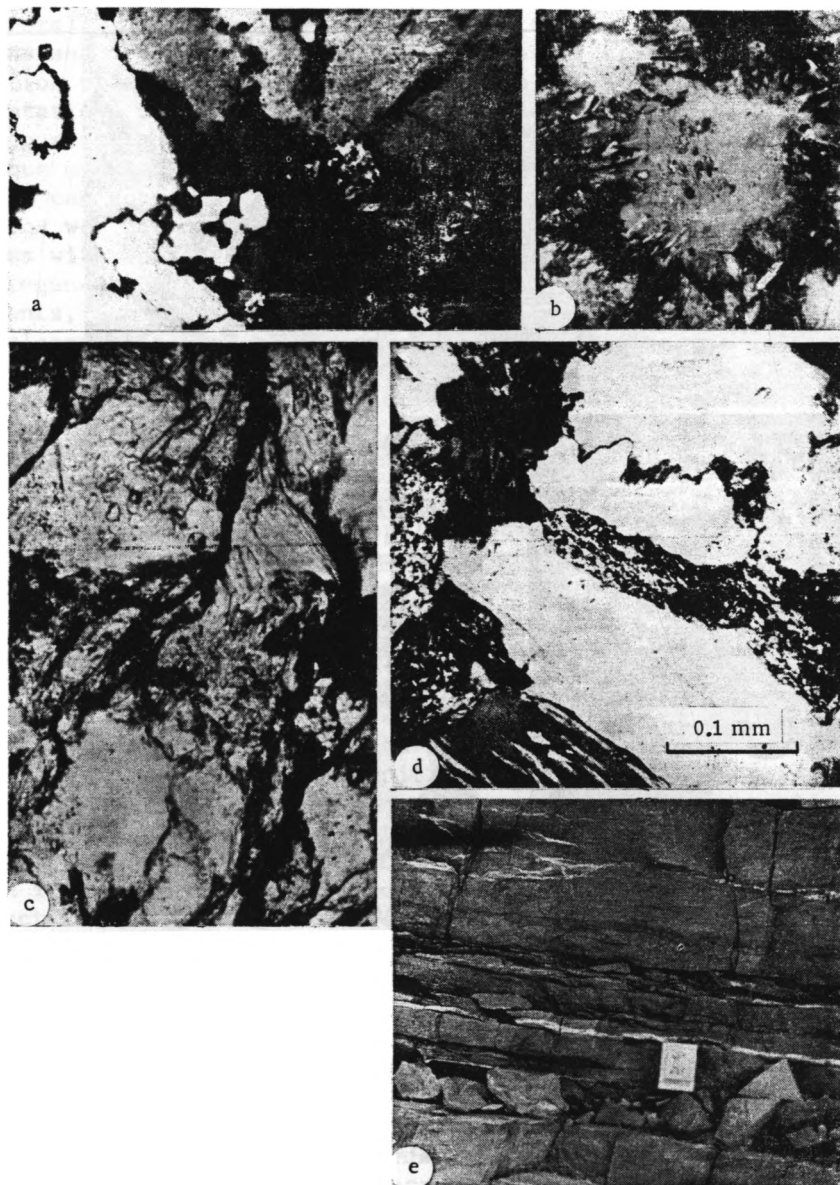


Fig. 2. Neomorphs of the metagenesis zone in sandstones of formations F-1 and F-2; photographs of polished sections with crossed nicols (a, b, d) and without analyzer (c) and outcrops (e); the scale of photomicrographs indicated in Fig. 2d: a) recrystallization-granulation blastases on contacts of quartz fragments pressed into one another; b) spikelike ingrowth textures of sericite lamellae in edges of regenerated quartz and feldspar fragments (Setachan suite, Middle Carboniferous; Orulgan ridge); c) differential slide textures in metasandstone of zone VII (same location); d) result of dissolution under pressure (microstylolitic sutures) and generation of quartz grains (Olenek stage, Lower Triassic; Bytantai rise); e) quartz veinlets in the same sandstone.

nodular lenses and thin interlayers, i.e., those that had been carbonitized in early catagenesis). Most others, as mentioned earlier, influenced the paragenetic associations of minerals in the cement according to the composition of their clastogenic components. For example, if the only source of SiO_2 was an alteration of clay minerals, there would be no direct correlation between the amount of terrigenous and authigenic regeneration quartz in the rocks of these formations. The common presence, in zones III-VII, of textures of gravitational corrosion of quartz fragments and skeletal silicates (see Fig. 1d and 2a, d) suggests that immense quantities of SiO_2 and other substances isolated by intralayer dissolution of minerals were redis-

tributed within sand beds. Fluids from clay formations could perform the important function of a solvent and a vehicle, i.e., operate as a catalyst determining the intensity of catagenetic processes. The specifics of lithogenetic zonality in this region, therefore, are not at variance with the basic scheme of elisional catagenesis. Since at least one-third of the section in the Verkhoyan complex consists of sandstones - and siltstones are even more widespread - their role in authigenic mineral formation becomes equivalent to that of clay rocks.

In the course of further evolution of sedimentary basins, at their maximum subsidence depth and during dislocations, intense thermobaric settings were created in which lithogenetic processes were now determined by new factors. The compaction of rocks attained its effective limit, the system of interconnected pores disappeared, and chemical reactions of mineral particles in a solid state began to be predominant; in particular, diffusion of ions to particle boundaries became more active. Basically new textures of recrystallization-granulation-blastases of zone VI developed; differential sliding textures of zone VII appeared as lenticular microblocks of strongly connected fragments and ingrowths of a sericite-like hydromica of polytype $2M_1$ placed obliquely with respect to the edges of these microblocks (see Fig. 2b, c). These neomorphs indicated that elisional processes had been replaced by entirely different reactions of mineral particles: diffusive-metastomatic reactions; in case of a high thermal activity these were recrystallization-blastic reactions. "The low-permeability rock blocks operated as reactors where dehydration occurred in the course of metamorphism of catagenesis. Faults of crack systems bounding these blocks were the collectors through which the water released in the process was transported" [13, p. 33]. The outflow of a portion of silica with this water was probably responsible for the massive development of a large number of alpine quartz veinlets, frequent in zones VII-VIII of alteration of the formation F-1 and F-2 (see Fig. 2d, e). Metalliferous components could travel along with silica, as suggested by correlation between the locations of ore shows and the occurrence areas of the above zones demonstrated by Andreev [1].

The evolution of lithogenetic zonality in space and time was largely controlled by the succession of closed and open hydrochemical systems. During the rapid sinking of miogeosynclinal formations, closed systems preserved the early catagenetic carbonate cement in sandstones and "stretched" (over several kilometers) the interval of the zones of deep catagenesis-early metagenesis (V-VI) in Kuranakh, Verkhneomoloi, and other sections of the F-1 formation, as opposed to the extremely slow rate of transition of these rocks to entities with balanced paragenesis of greenschist metamorphic minerals at depths greater than 15 km. As has been established [15], high partial CO_2 and H_2O pressures inhibit dehydration and decarbonitization and slow down the metamorphic processes. The appearance of the differential slide textures in zone VII can be compared with the process of microhydrorupturing and slating caused by chemical differentiation in the presence of a water fluid phase described in the closed hydrochemical system in the ultradeep bore hole being drilled on the Kola Peninsula [2]. Thermal effects during subsequent tectonic activations of the rock basin in these overwatered formations helped develop an open hydrochemical system; in areas of rupture, dislocations conducive to outflow of fluids metamorphic areas could begin to be formed; the process of metamorphism was completed in the Verkhoyan region after folding.

This spontaneous lithogenetic development of a set of terrigenous formations implies activation by thermal pulses from the depth; the sources of such pulses could be deep foci of paligenetic granitization. Their origin can be accounted for by a model of evolution of the fluid regime of asthenospheric protrusions and magmatic and metamorphic stages of intracontinental linear mobile belts suggested by Korotaev and Nikishin [9]. Theoretically, heat could also be generated during the formation of cover-overthrust structures (see calculations in [22]); however, judging by the fact that principal metamorphization fields in the Verkhoyan region tend to be close to faults with the outward thrust component rather than along overthrusts, the role of mechanical thermal pulses must have been secondary. Mantle fluids could be the main heat carriers. Thermal action upon rock matter brought into motion giant volumes of gas and water fluids concentrated in the rock basin.

The thermal anomalies of the Verkhoyan folded belt that gave rise to metamorphism are comparable to thermotectogenetic formations [21] in the Caledonides of the Sayan-Baikal region and in Scotland; they also bear resemblance to thermal anomalies in the Central Pamir, Talas-Alatau, and other areas [6, 18, etc.]. In the Verkhoyan region, metamorphism is less developed in modern erosional cuts than in the above-mentioned areas. This calls for defining the criteria of the initial signs (or the upper boundary) of metamorphism.

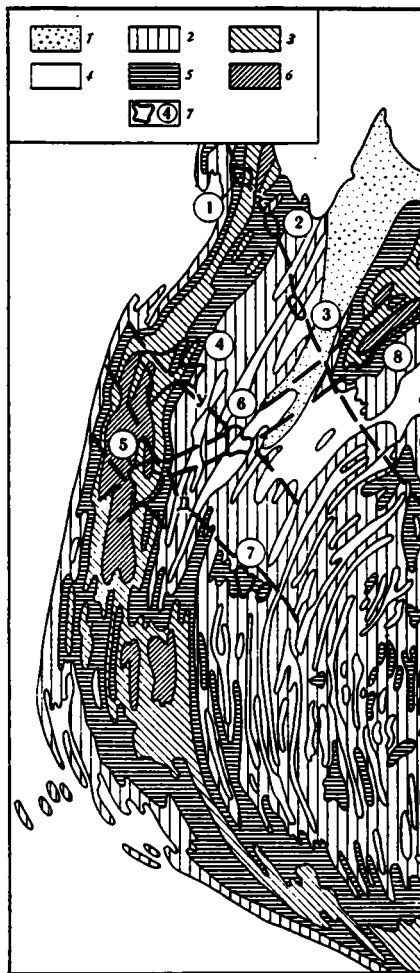


Fig. 3. Correlation of metamorphosed rock areas [36, 37] and the scheme of eroded strata compiled by Gusev [7] in the Verkhoyan-Kolyma folded system: 1) area covered by Cenozoic sediments; 2-6) strata of sediments eroded after Mesozoic folding, km (2-2; 3 - from 2 to 4; 4 - from 4 to 6; 5 - from 6 to 8; 6 - over 8; 7) outlines of metamorphism areas and their identification numbers (1 and 2 - upper reaches of Kharaulakh River basin, rocks P_1 - P_2 ; 3 - Araga-Yuryakh River, P_2 - T_2 ; 4) Ulakhan-Unguokhtakh River, C_2 - P_1 ; 5 - Abylychan, N'olon and Syncha Rivers, C_2 - P_1 ; 6 - Bukhuruk River, T_2 ; 7 - Betyugen River, P_1 - P_2 ; 8 - Kular ridge, P_2); dashed lines indicate zones of regional faults (B = Boguchan, U = Unguokhtakh, D = Dzhardzhan, etc.).

Relationships of Metagenesis and Metamorphism

Studies of mineral parageneses do not eliminate uncertainties from diagnosis of the upper boundary of metamorphism. Winkler [14], Logvinenko and Shvanov [14], Miyashiro [19], Gillen [5], Williams, Turner, and Gilbert [3], and many other investigators have concluded that this transition was gradual. Estimates of quantitative proportions of metamorphogenic minerals and relict clastogenic antities do not provide exact data. The author has demonstrated it with special reference to the Proterozoic of South Ulutau (Central Kazakhstan) in a study which revealed uneven alteration of the initial composition and textures of genetically different sand rocks in the greenschist facies [32].

This is only true, however, for evaluations based entirely on petrological data, because geologically different processes (regional deep subsidence and local rise of geotherms due to flows of fluids rising in dislocations) can originate similar or identical mineral paragenesis (such as in zones VI and VII). Soviet lithologists often refer to the origination stage of these paragenesis [12, 23] as metagenesis; outside the USSR it is described as the phylo-

morphous stage of diagenesis [40] or anchimetamorphism. The typical neomorphs include mineral associations of greenschist metamorphic facies, but in most rocks they are in metastable equilibrium, so that the number of mineral phases is greater than that of components (the Goldschmidt rule of phases is not observed). Metamorphogenic structures often precede the onset of an equilibrium state of mineral phases, whereas inverse relationships - with preservation of catagenic structures - sometimes occur in metamorphism.

Before we draw the boundary of metamorphism we must clarify the geologic aspects of the phenomena responsible for "metagenesis zones." In particular, the Verkhoyan region comprises two convergently similar types of alteration: 1) changes that gradually succeeded postcatagenetic processes in the deepest horizons of the rock formation basin, and 2) an external halo around weakening signs of zonal metamorphism of the amphibolite-greenschist facies, which is independent of the section thickness and is controlled by faults and deep sources of possible granitization of basement in the basin. A comparison with existing petrologic classifications of metamorphism shows that processes of the first kind are related to such concepts as static metamorphism [39], load metamorphism [8], and regional subsidence metamorphism [4, 38]. If we share this interpretation, the boundary of the onset of metamorphism becomes indefinite and stretched through a range of several kilometers. Alterations of the second kind correspond to the notion of dynamothermal metamorphism [8]; according to Marakushev [15, 16], they are the only true metamorphic processes. His theory that metamorphism occurs in folded systems at temperatures higher than the background (geothermal) levels of the corresponding depth facies and that they are associated with thermal anomalies in the earth's crust. In this interpretation, a metastable equilibrium of minerals is possible, because the concept of an equilibrium system in metamorphism is only valid as an approximation of reality. This interpretation, which is shared by the author [33], leads to the conclusion that at an early stage in studies of a folded region the term rocks of the metagenesis zone can be applied to all rocks with a metastable equilibrium of metamorphogenic minerals and secondary textures in zones VI-VII, understanding it as a morphological concept. At the next stage, distinctions are made between genetic categories: 1) metagenesis of the subsidence of a rock basin as a (postcatagenetic) lithogenesis stage; and 2) early metamorphic alteration of rocks superimposed on lithogenic change due to dynamic-thermal activation of the interior in a dislocation rock-forming basin. In different basins these processes may be of different origin: in the Verkhoyan region this kind of metamorphism is controlled by a system of ruptures, while in other folded areas it tends to occur near the axial zones of large faults (for example, in the Paleozoic geosyncline of South Tien-Shan [29]) or in sagging roofs of large magmatic bodies. Regardless of this, products of local metamorphism should be viewed as resulting from secondary rock alterations rather than the final lithogenesis stage.

It is practically impossible to distinguish them by studying isolated rock specimens of sections separately from the specific geological environments. Instead, we should map lithogenic zonation on the basis of formations. The main criteria for determining the onset of superimposed metamorphic alteration are sharp disconformities in boundaries of subformations and levels at which we see quartz blastases, spikelike sericite ingrowth textures, differential slide textures, and other postcatagenetic neomorphic signs that appear regardless of the paleodepth of rock in a dislocated basin; another indicator is a frequent transversely oriented alternation of these zones and zones with equilibrium mineral paragenesis of greenschist, amphibolite, and other facies of progressive metamorphism, occurring in disconformity to stratigraphic and formational boundaries.

These observations do not detract from the importance of studies of indicator features of minerals and mineral parageneses as important characteristics of metamorphism type in various geotectonic environments. Valuable data in this area have been obtained recently by Kossovskaya and Shutov [12]. The methodology suggested in the present paper can supplement and be combined with such studies. Relationships of catagenesis and metagenesis with regional metamorphism remain an important subject for investigation. Their study will require a comprehensive approach, with regional-geologic and precise in vitro analyses, which must be conducted on a genetic facies-formational basis.

LITERATURE CITED

1. V. S. Andreev, "Verkhoyan complex of Lena-Omoloi interfluvium (geology and distribution of ore mineralization)," Candidate's Dissertation, Geological-Mineralogic Sciences, Moscow State Univ. (1985).

2. L. V. Borevskii and A. A. Kremenetskii, "Geological role of groundwater during progressive metamorphism in open and closed systems," in: *Groundwater and Lithospheric Evolution (Proceedings of a National Conference)*, Vol. 2 [in Russian], Nauka, Moscow (1985), pp. 8-13.
3. H. Williams, F. Turner, and C. Gilbert, *Petrography* [Russian translation], Nauka, Moscow (1985), pp. 8-13.
4. H. Winkler, *Petrogenesis of Metamorphic Rocks* [Russian translation], Mir, Moscow (1979).
5. K. Gillen, *Metamorphic Geology* [Russian translation], Mir, Moscow (1984).
6. V. A. Glebovitskii, G. M. Drugova, Yu. V. Miller, et al., "Mesozoic tectonic-metamorphic evolutionary cycle of the Central and Southwestern Pamir," *Byul. MOIP, Otd. Geol.*, 58, No. 5, 37-49 (1983).
7. G. S. Gusev, *Folded Structures and Faults of the Verkhoyan-Kolyma Mesozoide System* [in Russian], Nauka, Moscow (1979).
8. N. A. Eliseev, *Metamorphism* [in Russian], Nedra, Moscow (1963).
9. M. Yu. Korotaev and A. M. Nikishin, "Evolution of the fluid regime of asthenospheric protrusions and stadiality of magmatism, metamorphism, and metallogeny of intracontinental linear mobile belts," *Dokl. Akad. Nauk SSSR*, 273, No. 2, 415-418, 1983.
10. A. G. Kossowskaya, "Mineralogy of the terrigenous Mesozoic complex of the Vilyui depression and the Western Verkhoyan region," *Tr. GIN Akad. Nauk SSSR*, No. 63 (1962).
11. A. G. Kossowskaya, "Problems of geomineralogy," in: *Studies in Lithology by the Geological Institute of the USSR Academy of Sciences* [in Russian], Nauka, Moscow (1980), pp. 110-158.
12. A. G. Kossowskaya and V. D. Shutov, "Types of regional epigenesis and early metamorphism and their correlation with tectonic settings in continents and oceans," *Geotektonika*, No. 2, 15-30 (1976).
13. I. G. Kissin, "Hydrodynamic conditions and geologic circulation of water in the earth's crust," in: *Groundwater and Lithospheric Evolution (Proceedings of a National Conference)*, Vol. 2 [in Russian], Nauka, Moscow (1985), pp. 31-34.
14. N. V. Logvinenko and V. N. Shvanov, "Characteristics of the boundary between sedimentary and metamorphic rocks," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 3, 36-45 (1973).
15. A. A. Marakushev, "Metamorphic facies series and geochemical metamorphism regimes," in: *Proceedings of the 26th International Geological Congress (Papers Presented by Soviet Geologists)* [in Russian], Nauka, Moscow (1980), pp. 51-58.
16. A. A. Marakushev, "Relationships of lithogenesis and metamorphism," in: *Clay Minerals in Lithogenesis: Conference Proceedings* [in Russian], Nauka, Moscow (1986), pp. 103-112.
17. Yu. G. Leonov (ed.), *Mesozoic Tectonics and Magmatism of Eastern Asia (Correlation of the Time of Tectonic Motion and Magmatism)* [in Russian], Nauka, Moscow (1983).
18. Yu. V. Miller, *Tectonometamorphic Cycles* [in Russian], Nauka, Leningrad (1982).
19. A. Miyashiro, *Metamorphism and Metamorphic Belts* [Russian translation], Mir, Moscow (1976).
20. N. I. Nenashev, *Magmatism and Development of Metalliferous-Magnetic Nodes in Eastern Yakutia* [in Russian], Nauka, Novosibirsk (1979).
21. I. E. Pavlovskii and M. Z. Glukhovskii, "The problem of thermotectogenesis," *Geotektonika*, No. 6, 38-52 (1982).
22. E. I. Patalakha and A. I. Polyakov, "Thermal effect of tectonic deformations," *Geol. Geofiz.*, No. 9, 14-22 (1977).
23. N. M. Strakhov and N. V. Logvinenko, "Sedimentary rock formation stages and their names," *Dokl. Akad. Nauk SSSR*, 125, No. 2, 389-392 (1959).
24. P. P. Timofeev, "Aspects of lithologic-facies analysis of sedimentary rocks," in: *Lithology and Geochemistry of Sedimentary Rocks and Ores (for the 75th Anniversary of Academician N. M. Strakhov)* [in Russian], Nauka, Moscow (1975), pp. 182-190.
25. P. P. Timofeev, "Formation: A genetically defined geologic body," *Litol. Polezn. Iskop.*, No. 3, 3-9 (1981).
26. P. P. Timofeev, "Problems of lithology," *Litol. Polezn. Iskop.*, No. 3, 3-13 (1987).
27. V. N. Kholodov, "Postsedimentary alteration in elisional basins (with special reference to Eastern Ciscaucasia)," *Tr. GIN Akad. Nauk SSSR*, No. 372 (1983).
28. V. N. Kholodov, "Formation of gas-water solutions in sand-clay strata of elisional basins," in: *Sedimentary Basins and Their Oil and Gas Prospects* [in Russian], Nauka, Moscow (1983), pp. 28-44.
29. V. N. Shvanov, *Lithoformational Correlations of Terrigenous and Metamorphic Strata (Southern Tien-Shan)* [in Russian], Leningrad State Univ. (1983).
30. V. D. Shutov, "Classification of terrigenous rocks and graywackes," *Tr. GIN Akad. Nauk SSSR*, No. 238, 9-29 (1972).

31. V. D. Shutov, "Mineral paragenesis of graywacke complexes," Tr. GIN Akad. Nauk SSSR, No. 278 (1975).
32. O. V. Yapaskurt, "Early metamorphic alteration of sandstones in geosynclinal Proterozoic sediments of the eastern side of the Maityube anticlinorium in Ulutau," in: Problems of Precambrian Sedimentary Geology [in Russian], Nedra, Moscow (1975), pp. 291-296.
33. O. V. Yapaskurt, "Relationships of catagenesis and early metamorphism," Vestn. Mosk. Gos. Univ., Ser. 4, Geol., No. 5, 33-38 (1982).
34. O. V. Yapaskurt, "Lithology of terrigenous formations of miogeosynclinal sedimentary rock basins of the Verkhoyan complex," Doctoral Dissertation, Geological-Mineralogic Sciences, Moscow State Univ. (1986).
35. O. V. Yapaskurt, "Sedimentogenesis and lithogenesis in miogeosynclinal basins," Vestn. Mosk. Gos. Univ., Ser. 4, Geol., No. 3, 18-30 (1987).
36. O. V. Yapaskurt and V. S. Andreev, "Zonal metamorphism and thermal domes in northern Verkhoyan region," Dokl. Akad. Nauk SSSR, 280, No. 3, 714-717 (1985).
37. O. V. Yapaskurt and V. L. Kosorukov, "Influence of faults on early metamorphic alteration of clay rocks in the western Verkhoyan region," in: Clay Minerals in Lithogenesis: Conference Proceedings [in Russian], Nauka, Moscow (1986), pp. 80-89.
38. D. S. Coombs, "Some recent work on the lower grades of metamorphism," Australian J. Sci., 24, 203-215 (1961).
39. R. A. Daly, "Metamorphism and its phases," Bull. Geol. Soc. Am., 28, 375-418 (1917).
40. E. C. Dapples, "Diagenesis of sandstones," in: Diagenesis in Sediments, G. Larsen and C. V. Chilingar (eds.), Elsevier, Amsterdam (1967), pp. 91-125.
41. R. J. Stewart, "Zeolite facies metamorphism in the Western Olympic Peninsula, Washington," Bull. Geol. Soc. Am., 85, 1139-1142 (1974).
42. P. van der Kamp, B. E. Leak, and A. Senior, "The petrography and geochemistry of some California arkoses with application to identifying gneisses of metasedimentary origin," J. Geol., 84, 195-212 (1976).

QUANTITATIVE EVALUATION OF SYNINVERSIONAL CATAGENETIC HYDRATION OF THE CARBONIFEROUS STRATA IN THE DONETS BASIN

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Prevalent views concerning epigenetic alterations of Carboniferous rocks in the Donets Basin are discussed. The sedimentary rocks of the basin are shown to have experienced, besides the regional alteration of subsidence catagenesis, an intense regional superimposed alteration that occurred during the inversional stage of catagenesis. The superimposed catagenetic alteration of clay minerals must have released immense amounts of water into the interstitial space. An estimate is computed of syninversional catagenetic hydration of the Carboniferous in the Donets Basin.

In [18], the widespread separation cracks in the sedimentary rocks of the Donets Basin have been proved to be hydraulic rupture cracks. They were caused by a secondary hydration of rocks in the basin because of syninversional catagenetic processes. In [18] the discussion centered on separation crack formation mechanisms; less space was given to causes and the scale of secondary hydration of the Carboniferous beds in the basin. These interesting and complex issues are discussed in the present paper with a greater specificity.

Time and Nature of Epigenetic Alterations of Sedimentary Rocks in the Donets Basin

Until quite recently, regional metamorphism of coal and rock epigenesis in the Donets Basin were believed to be entirely controlled by the depth of their preinversion subsidence and the respective lithostatic pressures and temperatures. In a summary analysis of the data

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on coal metamorphism patterns in the Donets Basin, Levenshtein [4] discovered an increase of metamorphism grade within a single coal seam (in sediments of an equal thickness) in proportion to its depth in the modern structural plan. Since tectonic structures could not have affected metamorphism before they were formed, Levenshtein rightly concluded that these facts are inconsistent with the view that metamorphism was completed before folding, which is placed at the boundary of the Lower and Upper Permian in the Donets Basin [4]. Convincing data in support of this conclusion were discovered by the author in the central part of the basin. Within the main anticline, the boundaries of the coal metamorphism zone cut sharply across the stratigraphic levees (Fig. 1). The facts discovered by Levenshtein [4] were justifiably taken as evidence of a two-stage alteration of coals in the basin. He linked alterations during the first stage with the coal subsidence depth in the sedimentary period of the basin's history. The second metamorphism stage was assumed to evolve "permanently," i.e., during the entire postinversional period in the development of the basin. Those parts of coal seams that are brought by large folded or overthrust deformations to far higher occurrence levels (in environments of lower pressures and temperatures) turned out to be less metamorphosed than the parts at greater depths.

The idea of a "permanent" metamorphism of Donets Basin coals was not accepted by a large number of authors [12, 13, 19]. Serious objections were advanced against it, including the doubts that coal matter after evolving through a stage of high temperatures and pressures could be altered at lower values of these parameters [11].

A clear correlation is known to exist between coal metamorphism grade and alteration of surrounding rocks [4, 11]. Under the hypothesis of "permanent" coal metamorphism, this implies that both coal and rocks in the Donets Basin experienced progressive alteration at thermodynamic parameters that had lower values (than before). Since progressive alteration of rocks in new settings with lower pressures and temperatures is impossible [15, etc.], Levenshtein's hypothesis concerning the alteration of these rocks, and therefore of the coals in this basin, should be rejected.

Several geologists [12, 19] tried to explain the intersections of isopachytes with isometamorphism surfaces by resurrecting Shatskii's [23] views of a synsedimentary nature of Donets Basin folds. According to this theory, the different degrees of metamorphism of coal seams in the arch and the sides of the main anticline and at the bottoms of adjacent synclines can be due to the initially different depths of their subsidence before inversion. On the other hand, Shirokov [24], and later other geologists [4], who studied in detail Carboniferous sediment accumulations and tectonic settings, showed that the theory [23] of a synsedimentary nature of Donets Basin folding is incorrect. These authors have proved convincingly with a more representative data sample [23] that there is neither a reduction of Carboniferous rocks toward anticline arches nor any regular correlation of facies and tectonic structure elements. If synsedimentary folded structures did develop in the Donets Basin, they must have been very low-angle bends of layers [13]. A critical review [10] of new data with arguments pro and con on the synsedimentary formation of the main anticline supports Shirokov's [24] view that this fold was founded during the Saalian phase of Hercynian tectogenesis, after accumulation of Carboniferous and Lower Permian strata. Levenshtein's observations are thus not supported by the synsedimentary folding hypothesis.

There is another view, first proposed by Dubinskii [7], concerning the nature of coal and rock alteration in the Donets Basin; we believe that it provides a most comprehensive and logical explanation for the entirety of the above-mentioned facts. According to [7], the energy of the thermal field acting upon the coal seam after it subsides to the maximum depth is insufficient for its entire metamorphism, but powers only the initial, relatively low coal metamorphization. The principal phases of coal metamorphism occurs immediately after the end of the sedimentational stage in basin development, i.e., during inversion. Dubinskii believed it to be due to a sharper upward jump of the geothermal gradient because of the rise of high-temperature subcrustal masses under the Donbass trough.

Dubinskii advanced this theory over three decades ago, but his views are cognate to the current models of regional progressive metamorphism of geosynclinal beds. A consensus view now holds that basic metamorphic rock alterations in these beds were associated with the inversional stage in the evolution of geosynclinal troughs. Progressive regional metamorphism of that type, unlike regional subsidence metamorphism, was caused by deep fluid flows and heat energy rising into the sedimentary cover [15, etc.]. However, the concept of two genetic types of regional alterations was based on data for deeply metamorphosed strata but until recently

were never extended to rocks belonging to epigenesis zones. Relatively recently, Yapaskurt [25] showed that regional epigenesis alterations can also be of a dual nature; regional epigenesis as well as regional metamorphism should thus be divided into two genetic types. Yapaskurt called one of these types "regional background alteration"; it results from the fact that sedimentary beds, as they subside, enter zones of higher temperatures and static pressures; the other type - "regional superimposed alterations" - is due to "thermal-dynamic rock activation." Like deeper alterations of thermal regional metamorphic rocks, changes of superimposed epigenesis are apparently connected with deep fluid and thermal energy flows rising into sedimentary strata.

Until a few years ago, there was no direct proof of Dubinskii's hypothesis of syninversional alteration of coal and rock of the Donets Basin. Due mainly to absolute age determinations of authigenic hydromicas and mixed-layer minerals from clay schists and argillites of the various Carboniferous sections, the hypothesis was confirmed directly. It was discovered that rock-forming minerals were formed there 230-240 million years ago [17], i.e., at the time of basin inversion and its principal tectogenesis epoch. In addition, epigenetic alteration of Donets Basin rocks is allochemical, meaning that it occurred in an open system [14]. A comparison of the chemical composition of contemporaneous rocks from various coal metamorphism zones indicated a substantial influx of certain elements and outflux of other elements during catagenesis. For example, in the transition from argillites of the zone of grade D coals to clayey schists of the zone of grade A coals, there is a consecutive increase of aluminum and alkali and a decrease of iron, magnesium, and water. These facts seem to indicate that, besides temperature and pressure, major agents of epigenesis were chemically active fluids, which brought petrogenic elements into the bed and redistributed them in it. Veins and veinlets of quartz, carbonates, dickite, gumbelite, and other minerals widespread in the Upper Paleozoic rocks but not in younger sediments are of a clear metamorphogenic origin; they may be evidence of strong syninversional catagenetic processes. Judging by their age correlations with elements of the folded structure in the basin, they must belong to formations of that stage. Finally, the fact that coal metamorphism (and rock epigenesis) boundaries cut across stratigraphic levels can also indicate syninversional processes of coal metamorphism (and rock epigenesis). Yapaskurt [25] believes that the fact that these surfaces cut across and along the course of tectonic structures is the main indicator of superimposed regional alterations.

Mikhalev [12], an exponent of the hypothesis of synsedimentary formation of the main anticline in the Donets Basin, has carried out a careful paleoreconstruction of the sedimentary strata and coal isometamorphism surface (OS/T boundary) by the onset of inversion in the basin. From the spatial position of isometamorphism surfaces he concluded that they have specific features probably reflecting "additional heating of the coal-bearing bed during the second metamorphism stage upon inversion of the thermal regime," as had been hypothesized by Dubinskii [12].

Syninversional Regional Catagenesis of Rocks in the Donets Basin

The above data indicate that the rocks in the sedimentary strata of the Donets Basin experienced, in addition to subsidence catagenesis, during its inversional stage, a superimposed regional catagenetic alteration. The purpose of the present study is to evaluate the amount of water released into the interstitial space of rocks by syninversional catagenetic processes; it is therefore necessary to separate from the background the alterations of rocks during subsidence epigenesis. To do so we will rely on the fact that in the central area of the Donets Basin, coal metamorphism zone boundaries cut across stratigraphic boundaries. As mentioned earlier, these relationships of boundaries are due to superimposed processes of syninversional epigenesis, which occurred in a sedimentary bed, by that time already distorted by (also syninversional [4]) major folding. As a result, different portions of the same bed were brought to different hypsometric levels, were subjected to different anomalous thermal fields and altered unequally. At present, the vertical section of the carbonic bed transverse to the principal anticline has convex surfaces of equal metamorphism (or isotherms) (see Fig. 1). The bend is obviously due to the continued growth of the fold after the extinction of syninversional metamorphic processes. A paleoreconstruction of the principal anticline for the time when these processes ended was conducted by reducing isometamorphism surfaces to a horizontal position and decreasing the slope angle of its sides by the corresponding value; this reconstruction indicates that the structure at that time was ~4 km high. The difference in hypsometric levels of parts of the same bed in the anticline arch and bottoms of adjacent syn-

clines was also 4 km. In the transverse section of this fold, shown in Fig. 1, we see, for example, that the coal seam k_5 of the Kamenka suite of the Middle Carboniferous has been metamorphosed in its arch only to gas coal grade. Toward the synclines and to the dip of the seam k_5 its metamorphism grade increases progressively, and at the bottom probably reaches anthracite metamorphism degree (in both instances, the depth of preinversional subsidence of the seam k_5 was the same - ~6-6.5 km). The intensity of catagenetic alteration in the rocks surrounding a coal seam varies similarly. In the anticline arch the alteration corresponds to middle catagenesis or the beginning of late catagenesis, while in the cores of the synclines it attains a level of metagenesis. Assuming that portions of the coal seam k_5 that at present make up part of the arch of the principal anticline developed their degree of metamorphism as early as in the preinversional prefolding time (i.e., that they did not experience superimposed alteration), we conclude that a deep alteration of the seam parts occurring at a lower hypsometric level in the section was entirely due to second-stage metamorphism. Subtracting the magnitude of background alteration of coal in the anticline arch from the degree of alteration of coal in the sides of the anticline, we can estimate the contribution of terminal metamorphism to side alteration. Likewise, taking the alteration of rocks in the arch for a "baseline" value, we can determine the relative contribution of syninversional epigenesis to the overall change of more altered rocks for almost any present degree of catagenesis. We should only bear in mind that the result will more likely reflect the action of superimposed epigenetic processes, because portions of the seam k_5 and surrounding rocks in the arch of the anticline could have also experienced such impacts.

We will examine the specific forms of superimposed epigenetic alteration of mineral matter of rocks in this basin. The Carboniferous of the Donets Basin consists of clay rocks, accounting for 70% [4]; most alterations during both stages of catagenesis should therefore affect clay minerals. Evolution of clay minerals and their associations during epigenesis have been studied in detail in the Donets Basin [8, 9, 11, 16]. With increasing rock catagenesis, clay minerals passed through a sequence of transformations (Fig. 2). In the long-flame coal area slightly altered clay rocks consist mainly of montmorillonite, mixed-layer units, and heavily hydrated hydromicas. In the gas clay areas the amount of montmorillonite declines, but mixed-layer minerals contain up to 70% of the swelling component. Amid fat coals, montmorillonite disappears, and the groundmass of clay rocks consists largely of mixed-layer formations, with a 50% swelling component. In the coking coal zone the smectite component drops to 10-40%. In the PA grade coal zone this amount drops even further. Finally, in the anthracite zone, clay schists consist mainly of hydromica of various degrees of hydration. The evolutionary series of clay minerals has been observed in many sedimentary basins of the world [9, 22, 26, etc.] with a universal regularity. This series and the data concerning the contribution of superimposed epigenesis into the general rock alteration indicate that the composition of clay sediments before the inversion through most of the strata was close to that observed currently in the development areas of the least altered rocks of long-flame and gas coals, i.e., that it was similar to the earliest members of this series. We see that the clay rocks of the basin, before epigenetic processes of the second stage, in a considerable range of depths, must have consisted mainly of montmorillonite, mixed-layer minerals with a high smectite content, and heavily hydrated hydromicas. Preservation of these minerals at great depths may seem unlikely. We will therefore briefly discuss the modern views about their conditions of epigenetic alteration.

Grimm [6] stated that montmorillonite-to-hydromica transformation (in the presence of the necessary amount of potassium) is possible only after montmorillonite loses interstitial water. Experimental work by Khitarov and Pugin [21] has shown that montmorillonite structure indeed can be rebuilt into hydromica only after it is dehydrated. These investigators also established that the release of interstitial water from montmorillonite packets is controlled mainly by temperature conditions in the earth's interior. Before the temperature at a given depth in a sedimentary bed has reached a certain level, the smectite component cannot be dehydrated and will not be converted to illite. The diagram constructed by these investigators from experimental data (Fig. 3) shows the maximum depth of possible existence of montmorillonite at various geothermal gradients. It indicates, in particular, that for a geothermal gradient of 10°C/km montmorillonite can survive in a hydrated state down to a depth of 16 km.

Deep drilling in the present sedimentary basins confirms this theory [21]. In the productive clay bed of the Baku Archipelago, with abnormally low temperatures, 40% and more montmorillonite has been established in the entire drilled section to a depth of 6200 m [3].

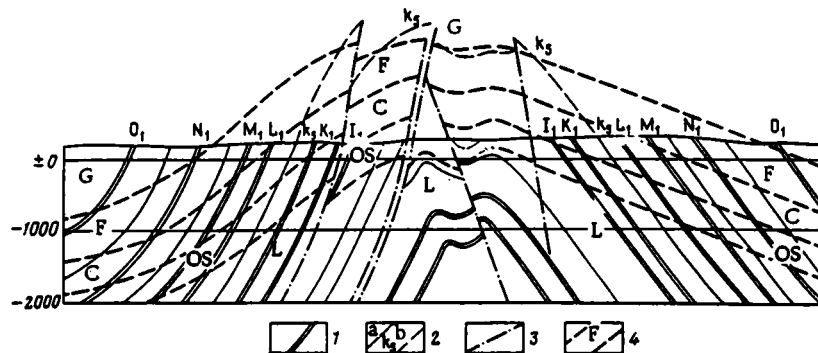


Fig. 1. Transverse section of main anticline with coal metamorphism zones (after Levenshtein with modifications): 1) limestone beds at boundaries of Carboniferous suites; 2) coal seams (a - in natural occurrence; b - eroded); 3) overthrusts; 4) metamorphism zone boundaries and coal grades.

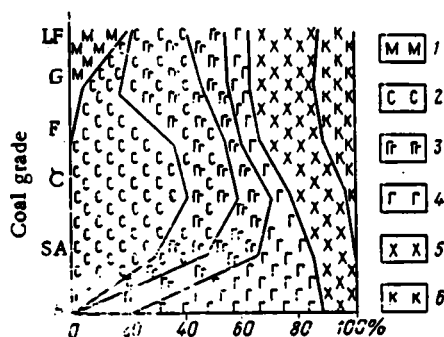


Fig. 2

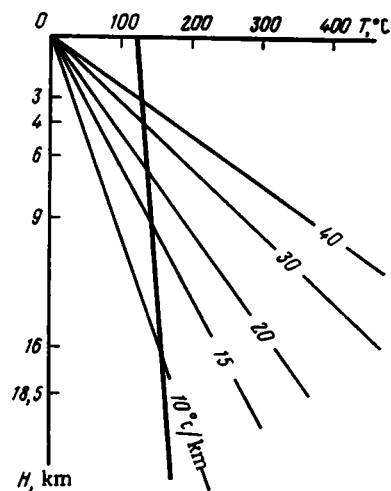


Fig. 3

Fig. 2. Distribution of clay minerals in clay rocks of the suite C_2^5 according to coal metamorphism zones (after Rekshinskaya): 1) montmorillonite; 2) mixed-layer minerals of montmorillonite-hydromica series; 3-4) hydromica (3 - heavily hydrated; 4 - weakly hydrated); 5) chlorite; 6) kaolinite.

Fig. 3. Depth of potential montmorillonite preservation (to the left of the bold vertical line) and hydromica formation from montmorillonite in the presence of potassium, depending on geothermal gradient (after Khitarov and Pugin).

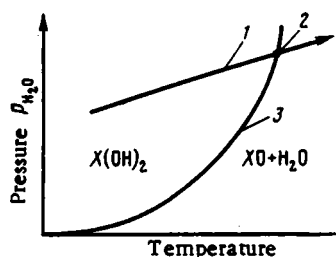


Fig. 4. P-T conditions of dehydration of water-containing minerals $X(OH)_2$ yielding anhydrous phase X and free H_2O : 1) geothermal gradient; 2) dehydration point; 3) vapor pressure curve.

This suggests that during the subsidence stage the interior in the Donets Basin had extremely low temperature gradients. Geothermal studies in depressions of modern inner seas (with sedimentary deposits comparable to the Upper Paleozoic strata in thickness and composition) show that a low-temperature regime in the earth's interior is typical for geotectonic structures of this kind. Thermal flows in such depressions have lowest values; temperature gradients are rarely greater than $15^{\circ}\text{C}/\text{km}$ [5, 20].

The causes of dehydration of minerals with the swelling phase mostly as a result of temperature have been studied in [26]. The weak effect of the rising external pressure on dehydration of clay minerals according to this study is due to the fact that the density of bound water in them is 20-40% higher than that of free water in volume. As water is removed from the mineral, the overcompaction factor ceases to operate and the volume increases abruptly. The inversion of water density would counteract external conditions when a mineral is exposed to pressure. The pressure growth (including interstitial pressure [3]) will prevent the release of overpressurized interplane water from the mineral. In the pressure conditions at the top of the earth's crust, the pressure is a factor containing or even stopping the dehydration reactions of the montmorillonite-hydromica mineral series. It is only after temperature rises that dehydration may begin (or resume). As long as temperature conditions have not reached the critical values for the given depth, the swelling phase will remain hydrated and will not be converted to hydromica.

This concerns dehydration of montmorillonite and mixed-layer minerals. Recently, however, Blokh [2] showed that dehydration of clay strata of a hydromicaceous composition is also determined largely by temperature conditions at depths. As with swelling minerals, the controlling factor is the overcompaction (to $1.4\text{--}2\text{ g/cm}^3$) of water bound in hydromicas. Finally, metamorphic reactions in coal matter should also include a volume growth (except for the earliest stages, B and E) as a result of separation of water and gases [4]. In that case, too, the rising geostatic pressure should be a factor slowing down the reactions.

Pressure and temperature effects on dehydration and degassing can be considered in a slightly different aspect [20]. Compounds consisting of a volatile and less volatile components are characterized by an equilibrium pressure of vapors of the volatile component. The pressure is mainly determined by thermodynamic parameters. Depending on the ratio of volatile component pressure and equilibrium pressure for given thermobaric conditions of the environment, a water-containing compound will either be preserved in a hydrated state or decomposed (Fig. 4). For example, if the external pressure of the volatile component at a given temperature will be higher than the equilibrium level, the water-containing mineral will remain hydrated regardless of depth. As the environmental temperature rises, the equilibrium pressure will also rise and may increase the external pressure of the volatile component. The mineral phase will then begin to decompose and release the volatile component.

Since the pressure of interstitial fluids in sediments of deep troughs (both recent and, apparently, the ancient analogs) starting from depths of 2-3 km approaches regularly the lithostatic pressure (abnormally high formational pressures) [5, 20, etc.], the volatile component pressure almost throughout the section of such troughs should be close to or equal to the lithostatic pressure. The dehydration of water-containing minerals at any depth should thus begin only after the geothermal gradient crosses the curve of equilibrium vapor pressure (see Fig. 4).

Theoretical, experimental, and in situ observations indicate that the coal-bearing strata of the Donets Basin before the inversion may have consisted, in a broad range of depths, of montmorillonite and mixed-layer minerals with a high concentration of swelling packets. Much of alterations of clay matter in the basin was associated with an additional heating that occurred during the inversional stage. This theory is supported by the results of potassium-argon dating, mentioned earlier [17]. Potassium-containing minerals are subjected to a thermal treatment for release of radiogenic argon-potassium and water-containing minerals (for example, hydromicas) are heated, argon and water are released almost simultaneously because of the similarity of their activation energies [1].

The absolute age of hydromicas from clay members of the various sections (depths) of the Donets Basin Carboniferous coincides and is the same as at the time of inversion [17]. This suggests that the sedimentary strata of the basin about that time experienced a thermal "excitation," which brought out argon from the crystal lattice of hydromicas and turned on the geochronological clock. That would also mean that it was a time of dehydration and alteration of clay minerals.

TABLE 1. Water Contents in Donets Basin Clay Minerals,
%

Mineral	H ₂ O-	H ₂ O+	Total
Montmorillonite	13,44	6,66	20,1
Hydromica	0,65	6,85	7,5
Kaolinite	1,11	13,15	14,26
Chlorite	0,43	9,58	10,06

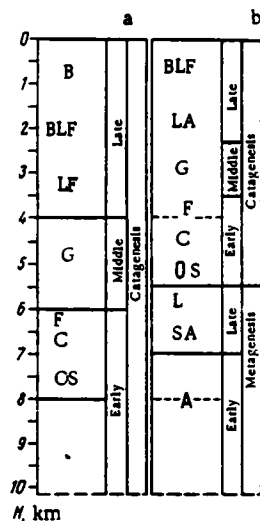


Fig. 5. Positions of the boundaries of rock epigenesis zones and coal metamorphism zones in the Carboniferous of the Donets Basin before (a) and after (b) inversion (in the latter case, in a setting of low angle occurrence of seams).

In summarizing, we can say that the sediments of the Carboniferous in the Donets Basin during its inversional evolution were subjected to superimposed catagenetic alteration as a result of the additional thermal impulse. These alterations throughout all catagenetic stages must have been accompanied by almost continuous release of chemically and physically bound water from clay minerals. In an environment of (geologically) fast syninversional catagenetic processes, the release of water from immense volumes of clay rocks would inevitably result in a general secondary hydration of the Carboniferous in the Donets Basin.

Estimation of the Secondary Hydration of Donets Basin Rocks

For a quantitative evaluation of the secondary hydration of rocks in the basin we will use the data [8, 16] concerning the approximate contents of clay minerals in these rocks (see Fig. 2) and the contents of adsorptional and crystallization water in these minerals (Table 1). Based on these data, we have estimated that a metric ton of clay rocks from the gas coal zone (middle catagenesis) contains ~136 kg of water of these types. A metric ton of rocks from the coking coal zone (late catagenesis) contains 124 kg of thaw water; the rocks in the PA coal (early metamorphism) contain 106 kg. Finally, in the anthracite zone (late metamorphism), where hydromicratization of the swelling phase has been completed, clay schists contain less than 80 kg of water. From these data one can readily calculate the amount of water released from a metric ton of clay rocks in each stage of their catagenesis. In particular, the alteration of 1 ton of clay rocks of the middle catagenetic stage (coal zone of grade G) to the late catagenetic (coals of grades F, C, and OS) would release into their interstitial space some 12 kg of water. The further alteration of these rocks to early metamorphism (T, SA coal zone) should release into their interstitial space an additional 18 kg of water; the alteration to late metamorphism (anthracite zone) would provide 26 kg more. A total of 44-56 kg would be thus released from each metric ton of deep-altered rocks during the second stage of catagenesis. This may not seem much, but it has been estimated that the interstitial space would have to expand some 10% to hold this regenerated water.

One can estimate the amount of water released by a 1 m² rock column in a depth interval of 4 to 8 km. Data suggest that before the beginning of the second catagenesis stage, the lower boundary of the long-flame coal zone lay at 4 km, gas coal at 6 km, and coking coal at 8 km (Fig. 5a). Syninversional epigenetic processes in the 4-km interval would alter the top 1.5 km of gas coal zone (middle catagenesis) to late catagenesis (coal grades F, C, OS), (coals T and PA). The rocks of the upper half of the zone of metamorphism of coal grades F, C, and OS (middle catagenesis) were in turn altered to the stage of early metagenesis (T and PA), and those of the lower half to the stage of late metagenesis (anthracite zone of coal metamorphism) (Fig. 5b). We have calculated that these alterations must have squeezed out of a 4-km rock column with an average density of 2500 kg/m³ about 240 tons of water. Since clay rocks in the Donets Basin constitute about 70% of the total volume, the number should be reduced to 150-170 tons. Although these are approximate estimates, they should represent correctly the order of magnitude of syninversional increase of the amount of interstitial water. It is interesting to evaluate the amount of water released during the inversional stage from the entire sedimentary massif of the Donets Basin. Assuming that its total volume is $7.5 \cdot 10^5$ km³ ($15 \times 100 \times 500$ km), the amount of water released from Donets Basin rocks in that period could be as large as $30 \cdot 10^{12}$ tons. This is comparable to the size of the Caspian Sea ($75 \cdot 10^{12}$ tons). These estimates, and calculations by other investigators [22], show that the second stage of dehydration of clay beds in large sedimentary basins is a major geologic event.

Even if these figures overestimate the amount of newly formed water (probably because of an overestimated amount of clay minerals in rocks), we should consider that they do not include all the water released from minerals during epigenesis. In addition, the calculations should take into account the volumes of various gases released in large quantities into the interstitial space of rocks, such as during degassing of coals and carbonates and the fluids that intruded into the sedimentary bed from the depths.

Calculations show that during the inversional stage of evolution of the Donets Basin, rocks must have experienced a general secondary hydration. The gigantic scale of this process suggests that it could lead to major tectonic deformations, as well as to the development of numerous hydraulic rupture cracks.

LITERATURE CITED

1. N. N. Amshinskii and V. N. Melenevskii, "Interrelationships between dehydration and release of argon by micas at heating," Tr. Zap.-Sib. Otd. Vsesoyuz. Mineral. o-va, No. 3, 10-14 (1976).
2. A. M. Blokh, "The universal applicability of the Powers and Burst sedimentary dehydration model," Izv. Akad. Nauk SSSR, Ser. Geol., No. 6, 119-124 (1977).
3. L. A. Buryakovskii and R. D. Dzhevanshir, "Interconnections and reciprocal influence of alteration of clay minerals and thermobaric conditions in the interior," Geokhimiya, No. 4, 512-521 (1986).
4. I. A. Kuznetsov (ed.), Geology of Coal and Bituminous Shale Deposits in the USSR, Vol. 1 [in Russian], Gostoptekhizdat, Moscow (1963).
5. M. A. Goncharov, "Folding as a result of excess hydration of geosynclinal sedimentary beds before and after metamorphism," Vestn. Mosk. Gos. Univ., Ser. 4, Geol., No. 2, 14-23 (1983).
6. R. E. Grimm, Mineralogy of Clays [Russian translation], IL, Moscow (1956).
7. A. Ya. Dubinskii, "Metamorphism (geotectonic premises of coal metamorphism)," Geol. Zh., 12, No. 1, 11-15 (1952).
8. G. V. Karpova, Clay Minerals and Their Evolution in Terrigenous Sediments [in Russian], Nedra, Leningrad (1972).
9. A. G. Kossowskaya, N. V. Logvinenko, and V. D. Shutov, "Formation and alteration stages of terrigenous rocks," Dokl. Akad. Nauk SSSR, 116, No. 2, 293-296 (1957).
10. M. T. Kucherenko, D. P. Filippov, and S. D. Pozhidaev, "Correlation of the thickness of the Carboniferous rocks and folded structures of the Donets Basin (a comment on articles by V. G. Belokon and A. K. Mikhalev)," Geotekhnika, No. 5, 126-134 (1971).
11. Coal Metamorphism and Epigenesis of Surrounding Rocks [in Russian], Nedra, Moscow (1975).
12. A. K. Mikhalev, "Reconstruction of the Donets Basin trough in connection with synsedimentary tectonic motions," Byull. MOIP Otd. Geol., 47, No. 3, 110-116 (1972).
13. V. N. Nagornyi and Yu. N. Nagornyi, "Variation pattern of the thickness of Carboniferous sediments in the Donets Basin based on recent data," Izv. Akad. Nauk SSSR, Ser. Geol., No. 1, 120-128 (1972).

14. N. A. Oveisi and O. P. Sharkin, "A study of the mineral composition of clay schists in the Donets Basin with an electron microprobe," *Geol. Zh.*, No. 5, 74-80 (1968).
15. A. A. Marakushev (ed.), *Petrography, Part 3* [in Russian], Moscow State Univ. (1986).
16. L. G. Rekshinskaya, "Alteration of clay minerals in the rocks of the Kamenka suite during the epigenesis," *Mineral. Sb.*, No. 27, Iss. 2, 172-177 (1973).
17. N. P. Semenko, B. B. Zaidis, and N. A. Oveisi, "Use of hydromica minerals and feldspars to study the time of catagenesis of clay schists and sands," in: *Dating of Ancient (Catarchean) Geological Formations of Basic Rocks* [in Russian], Nauka, Moscow (1967), pp. 117-122.
18. G. A. Solov'ev, "Origin of separation cracks in Carboniferous sediments of the Donets Basin," *Geotektonika*, No. 5, 91-101 (1985).
19. V. F. Tkachenko, "Metamorphism of coals in the Donets Basin," *Geol. Zh.*, No. 6, 142-147 (1969).
20. W. Pfaff, N. Price, and A. Thompson, *Fluids in the Earth's Crust* [Russian translation], Mir, Moscow (1981).
21. N. I. Khitarov and V. A. Pugin, "Montmorillonite at high temperatures and pressures," *Geokhimiya*, No. 7, 790-795 (1966).
22. V. N. Kholodov, *Postsedimentary Alterations in Elisional Basins* [in Russian], Nauka, Moscow (1983).
23. N. S. Shatskii, "Origins of the Donets Basin," *Byull. MOIP, Otd. Geol.*, 15, No. 4, 326-346, 1937.
24. A. Z. Shirokov, "Thickness of the Carboniferous in the Donets Basin," *Sov. Geol.*, No. 12, 41-54 (1938).
25. O. V. Yapaskurt, "Types of postdiagenetic alteration of terrigenous strata of the northern Verkhoyan region and adjacent territories," in: *New Developments in Modern Lithology*, G. F. Krashenninnikov et al., (eds.) [in Russian], Nauka, Moscow (1981), pp. 51-55.
26. J. F. Burst, "Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration," *Bull. Am. Assoc. Petrol. Geol.*, 53, No. 1, 73-93 (1969).

GENETIC TYPES OF SCANDIUM DEPOSITS

L. F. Borisenko

UDC 550.4(552.2)

Scandium has been established as an impurity in ores from deposits of various genetic types. Of most practical interest is the occurrence of scandium in titanium, iron, aluminum, uranium, and phosphate ores, most of which are of an exogenous origin.

After its discovery by Nielson in 1879 scandium remained without any practical use for nearly 100 years. In the last decade several applications have been found. Scandium-containing ferrites have been used in computer devices. Ge-Gd-Sc garnets are used in the latest-generation computers, and Ga-Sc-Gd garnets may be used in the laser industry. High-intensity mercury lamps with a scandium iodide additives are commonly used in light engineering. A high-temperature ceramic material has been produced from scandium and calcium oxides and from Sc_2O_3 and ZrO_2 . Metallic scandium is used as a neutron filter in nuclear reactors for material testing. Phoscan, $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$, is a promising compound that can be used as a highly conductive solid electrolyte. Properties of solid electrolytes fabricated by baking a mix of Sc_2O_3 , ZrO_2 , and Al_2O_3 at 1700°C are being investigated. Engineers have described the possible applications of scandium as a material in missile and aircraft building and space research due to its low density (3.02 g/cm^3) and a low melting point (1539°C). Aluminum alloys doped with scandium have been obtained (0.2-4% Sc) which are four times as strong as pure aluminum. There are promising applications of scandium in electronic engineering, solar power production, chemical engineering, and other fields.

These examples show that the era of scandium has begun. Its future hangs on the availability of sufficient amounts of natural resources and efficient processes for extraction of

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TABLE 1. Genetic Types of Scandium Deposits

Deposit group	Deposit type	Main commercial components	Sc content in ore, wt. %	Principal scandium concentrating minerals (Sc content, wt. %)
Magmatic	Ilmenite, ilmenite-titanomagnetite in gabbro-anorthosite, gabbro, gabbro-norite, and troctolite	Ti, P, Fe	0.002-0.003	Ilmenite (0.007-0.15); clinopyroxene (0.01-0.03)
	Titanomagnetite in pyroxenite, hornblende, and olivine	Fe, V	0.007-0.013	Clinopyroxene (0.008-0.02); hornblende (0.005-0.02); olivine (0.0002-0.015)
Contact metasomatic (skarn)	Mica-magnetite-fluorite with chrysoberyl	Fe, Be	0.005-0.02	Ferrimuscovite (less than 0.4); beryl (up to 0.07); helvite (up to 0.07); muscovite (up to 0.07)
Greisen	Wolframite and cassiterite, sometimes with beryl	W, Sn, Be	0.001-0.02	Wolframite (0.003-0.25); cassiterite (0.003-0.13); beryl (0.003-0.13); muscovite (0.005-0.05)
Hydrothermal	Quartz-muscovite metasomatites with pseudobrucite	Be	-	Pseudobrucite (0.48); beryl (0.34); bixbyite (0.23); hematite (0.1)
Weathering and placers	Crusts of weathering, with ilmenite, anatase, and rutile (residual)	Ti	0.0015-0.004	Ilmenite (0.005-0.01); kaolinite (0.005); anatase ($\sim$ 0.01)
	Alluvial, alluvial-lacustrine, and alluvial-diluvial with ilmenite and rutile	Ti	0.002-0.006	Ilmenite (0.005-0.015)
	Littoral-marine ilmenite, leucoxene, rutile, and zircon (ancient and recent) deposits	Ti, Zr	0.002-0.01	Ilmenite (0.004-0.01); zircon ($\leq$ 0.03-0.12); monazite (under 0.03)
Sedimentary	Bauxite	Al	0.0006-0.01	Boehmite (0.006-0.01); gibbsite (0.005-0.007); diasporite (under 0.003); magnetite (under 0.003); ilmenite (under 0.02)
	Phosphorite	P	0.0001-0.01	Carbonate-fluorapatite (under 0.02)
	Goethite-hydrogoethite, hydrogoethitic, etc.	Fe	0.001-0.01	-
	Bituminous and brown coal	C	0.0005-0.04 (in ash)	-
	Uranium-bearing sandstone	U, V	0.001-0.01	Metatuyamunite, hendersonite, and simplotite (0.005-0.01)
Metamorphogenic	Uranium-bearing quartzitelike conglomerates	U	$\sim$ 0.006	Brannerite ($\sim$ 0.05)
	Ilmenite-magnetite in gabbro-amphibolites	Fe, Ti	0.003-0.005	Ilmenite (0.007-0.01)

this rare metal. In the last few years the price of metallic scandium on the international market has been high, at a level of \$8/g, with distilled scandium costing as much as \$15-25/g. The high price of scandium is largely due to the limited uses of scandium raw materials.

Since Sc is a typical dispersed element, no large accumulations of scandium minerals of a commercial value have been found as yet. The true scandium minerals that have been discovered (thortveitite, basite, jervisite, cascandite, and kolbeckite) belong to the group of rare or very rare minerals. Pegmatites with thortveitite, found in Norway and Madagascar, have been discovered only in small deposits [2]. There is no reason to expect any considerable extraction of true scandium minerals in the future. The principal sources of scandium on a com-

mercial basis at present and in the foreseeable future will be ores of other elements, especially those in large deposits. Scandium is typically contained as an impurity (usually 0.005-0.03%) in a limited number of mineral ores. For producing scandium as a byproduct (in modern technology), titanium, iron, aluminum, zirconium, and uranium ores, as well as phosphate and some other raw materials, are important. Several principal genetic types of scandium-rich ore deposits are distinguished: 1) magmatic, 2) contact-metasomatic, 3) greisen, 4) hydrothermal, 5) weathering and placer types, 6) sedimentary, and 7) metamorphogenic (Table 1). This classification describes the deposits which have already been used as a source of scandium or for which methods of its extraction have been developed [15, 16]. The scandium prospects of most types of these deposits have been studied by the author. Scandium was determined by the Institute of Mineralogy, Geochemistry, and Crystallochemistry of Rare Elements with the use of neutron-activation analysis (analysis Yu. I. Sotskov, S. M. Lyapunov, and V. I. Chudinov); the detection limit was 0.5 g/ton Sc [1, 6].

Magmatic deposits are large in terms of the amounts of scandium. The main useful components are iron and titanium. The principal minerals that concentrate scandium are ilmenite (up to 0.015% Sc) and clinopyroxene (up to 0.03% Sc). Spatially and genetically, scandium-rich magmatic deposits are associated with basites and ultrabasites. The principal formations are: dunite-pyroxene-gabbro, alkaline-ultrabasite with carbonatites, gabbro-anorthosite, and gabbro-diorite-diabase formations. In magmatic deposits ores are mostly of a complex type, with commercial amounts of titanium, iron, vanadium, and sometimes phosphorus [3, 11]. The largest scandium-rich magmatic deposits were formed during the Precambrian and the Early Paleozoic.

Among endogenous iron deposits, the best scandium prospects are offered by titanomagnetite deposits in pyroxenites (dunite-pyroxenite-gabbro formations and uranium). The principal scandium-rich minerals are diopside and hornblende (0.01-0.02% Sc). Titanomagnetite contains $\leq 0.002\%$ Sc. Silicates account for 80-90% of all scandium content in ores. Most Sc in the production of titanomagnetite concentrate accumulates in silicate tailings, which are the potential source of its extraction [9].

In the ores of the deposits of alkaline-ultrabasic formations with carbonatites, higher scandium contents have been observed [2, 7] in pyroxene and olivine (up to 0.015% Sc), perovskite (up to 0.02%), and also in hatchettolite and baddeleyite (up to 0.07% Sc; the Kola Peninsula). Carbonatites of Southern Norway [18] contain accessory thorveitite, scandium-rich columbite (1.78% Sc), and niobium rutile (up to 0.04% Sc). There are plans to produce scandium as a byproduct in niobium extraction.

Scandium-rich ores of endogenous titanium deposits tend to occur mainly in gabbro-anorthosite (the Ukraine) and gabbro-diorite-diabase (the Ural) formations. Titanium ores of endogenous deposits are represented by basites (0.002-0.005% Sc). Ilmenite is the principal scandium concentrator (0.006-0.015% Sc). In disseminated ore, ilmenite contains up to 40-60% of the total ore scandium. The scandium content of ilmenite in gabbro-anorthosite formations typically depends on the basicity of the surrounding eruptive rocks. With increasing acidity of ilmenite rocks Sc concentration in the mineral declines (Table 2). Besides scandium, ilmenite contains impurities of V, Ta, Nb, Zr, Hf, rare earth elements, and Th. Extracting these elements as byproducts is a valuable aspect of ilmenite concentrate production [4]. Another mineral that concentrates scandium in titanium ores is clinopyroxene (up to 0.024% Sc), which may contain up to 50% of scandium in the ore. In plagioclase, Sc concentrations do not exceed 0.0002%.

Contact-metasomatic (skarn) iron ore deposits typically have a low scandium content. For example, the massive ores of skarn deposits in the Urals have average scandium contents of 0.0004% (based on 16 samples); in dispersed ores it is 0.0008% (based on 23 samples). Scandium concentration in magnetite is $\leq 0.001\%$; in pyroxene $\leq 0.004\%$. On the other hand, beryllium-rich micaceous-fluorite-magnetite skarns (Kazakhstan) have higher scandium contents, according to Zasedatelev. Ferrimuscovite from these skarns contains up to 0.4% of Sc; beryl, helvite, and muscovite, up to 0.07%. An inexpensive method of scandium extraction from micaceous formations has been suggested in the United States [23].

In greisenized deposits high scandium contents may occur in ores. Typically, higher scandium concentrations are found in wolframite (up to 0.25%) and cassiterite (up to 0.13%) in the ores that contain topaz [2, 17, 22]. A presence of scandium has also been described in beryl (up to 0.13%) and micas (up to 0.05%). Genetically, scandium-rich greisen deposits are associated with high-alkaline leucocratic granites. They are mostly of a Permian-Triassic age (less frequently, Mesozoic). Scandium reserves in greisen deposit ores are limited.

TABLE 2. Scandium Content in Ilmenite From Endogenous Deposits of Gabbro-Anorthosite Formations (Ukraine)

Metaliferous rock	Number of samples	Sc content, g/ton	
		range	mean
Melanotroctolite	34	81-100	88,4
Troctolite	63	70-100	82,1
Gabbro	138	58-100	80,6
Gabbro-norite	79	58-99	74,0
Gabbro-monzonite	25	46-61	52,0

Higher scandium contents have been reported in certain beryllium-bearing metasomatites in which fluorite and sometimes topaz play a considerable role. For example, in quartz-muscovite apoferruginous metasomatic deposits of the Thomas Range (Utah, USA) scandium has been found in pseudobrucite (0.48), beryl (0.34), bixbyite (0.23), and hematite (0.1). Beryllium ores are associated with rhyolites and tuffs of the Spear Mountain formation [19].

Residual (from weathering) and placer-type scandium deposits are fairly common. Titanium and zirconium deposits are of greater value in terms of scandium extraction. Residual deposits may contain substantial amounts (up to 200-500 kg/m³) of ilmenite, leucoxene, and anatase. The highest scandium level (up to 0.015%) has been observed in these minerals of residual deposits, formed after destruction of basic and ultrabasic rocks (see Table 2). Ilmenite from crusts of weathering developed on Ukrainian gabbroids contains 0.007-0.01% Sc. Scandium accumulates (up to 0.009%) in the upper kaolinitic zone of the weathering profile [6], especially on its ferruginated portions. Iron hydroxide is known to be a good scandium sorbent. A higher scandium content (0.003-0.004%) has also been observed in nickel-rich crusts of weathering formed after ultrabasic. Sc accumulation is also typical for ferruginous montmorillonite and ferrihalloysite of these crusts.

Ilmenite of alluvial and alluvial-diluvial placers formed from erosion of basite and ultrabasic crusts also has relatively high scandium concentrations ($\leq 0.01\%$). The scandium contents of the ilmenite in these placers and the parent crusts of weathering are nearly similar (0.008-0.01%). In both types scandium concentration rises slightly in the most leucogenized ilmenite [5]. Ilmenite of littoral-marine placers contains on average less scandium (0.002-0.07%), because rocks of uneven basicity were the source of material for this mineral (Table 3). Metamorphic rocks [12], often with a lower scandium content, could have played an important role. Besides ilmenite, minerals of littoral-marine placers that may be of interest for scandium extraction are zircon (up to 0.12%) and monazite (up to 0.03%).

Bauxites (residual and redeposited) regularly contain scandium (0.0006-0.01%). Highest contents are observed in bauxites formed from decay of basite, ultrabasic, basic effusives, and tuffogenic sandstones [10, 11]. Bauxites formed from weathering of acid and alkaline rocks contain little scandium ($\leq 0.001\%$). Ferruginous bauxites generally have a high scandium content. In specific deposits scandium concentration is more or less constant for each lithologic variety. On average, bauxites from various parts of the USSR according to our data contain 0.0004% Sc (540 samples); Ural bauxites, according to Gutkin, contain 0.0048%; and Kursk Magnetic Anomaly bauxites, according to Burkov and Chekhovski [10] contain 0.0026% (211 samples). In the Kursk Magnetic Anomaly, bauxites were formed mainly from disintegration of schists, which had a lower scandium content (0.013-0.0015%).

When bauxites are processed by Bayer technology, all scandium passes into red slurry, which has a concentration higher than bauxite by a factor of 1.5-2. The slurry (as well as belitic slurry) is a potential source of scandium. Highest scandium concentrations (0.028%) have been observed in the magnetic fraction of red slurry. Besides scandium, V, Ti, Zr, Ga, and rare earth elements can be extracted from bauxites as a byproduct.

Phosphate materials usually have low scandium contents. Phosphorites from several deposits (Aksai, Dzhanatas, Chilisai, Toolse, Egoryevsk, etc.) have 0.0001-0.001% Sc. Little scandium (0.0001-0.0005%) is found in apatite of endogenous and residual deposits. On the other hand, bone detritus of fossil fish consisting mainly of carbonate-fluoroapatite contains 0.01-0.02% Sc. The value of the detritus is enhanced by the presence of rare earth elements (up to 4.7% TR₂O₃) and uranium. On average, bone detritus concentrate contains 0.5-0.9% of

TABLE 3. Scandium Content in Ilmenite From Placers and Crusts of Weathering

Deposit type	Number of samples	Sc content, g/ton	
		range	mean
Crusts of weathering on basic rocks	57	76,8—96,7	85,8
Alluvial placers	27	79,3—98,0	87,8
Littoral-marine placers:			
recent	5	23,5—35,0	27,5
ancient	33	26,0—77,0	44,7

TABLE 4. Scandium Content in Sedimentary and Residual Iron Ores

Type of iron ore deposit	Mineral ore type	Structural ore features	Number of samples	Sc content, g/ton	
				range	mean
Marine	Hydrogoethite-leptochlorite-siderite	Oolitic (cemented)	17	9.6—28.0	15.8
Fluvial	Hydrogoethite-siderite-chlorite	Oolitic (sandstone)	29	6.8—11.7	9.0
Lacustrine-palustrine	Hydrogoethite-chlorite				
	Hydrogoethite-hematite	Ochreous-clayey	3	26.1—37.2	31.6
		Rubble-pebble	7	13.9—83.0	48.0
	Hydrohematite	Clayey	5	45.8—57.0	52.4
Residual	Goethite-hydrogoethite	Nodular	13	0.8—18.0	3.9
	Same	Nodular and ochreous	4	1.3—6.8	3.7

rare earth elements and up to 0.015% Sc [11]. Bone detritus accumulations (fish skeleton remains) are quite common in the Neogene of the southern European and Asian USSR.

Phosphate clayey schists may contain up to 0.05% Sc (Utah, USA). Permian phosphorites of the Phosphoria formation in the United States generally contain just 0.001% Sc [20]. In addition, they contain 0.03% La, 0.1% Y, and 0.001% Yb. Extracting scandium from phosphate material is cost-effective only if it is produced along with other rare elements. By extraction, Sc, REE, U, Sr, and F can be produced from poor phosphorites [13].

Sedimentary iron ore may contain higher amounts of scandium (sometimes up to 0.01%). This is mostly true of ores formed from decay of basic and ultrabasic rocks. It also applies to lacustrine-palustrine, fluvial, and marine sedimentary iron ores. In lake-swamp ores of the Ural with a spatial tendency for association with ultrabasites, we have discovered approximately 0.005% Sc (Table 4). Highest concentrations (up to 0.02%) have been observed in the clay component of rubble-clay ores formed by pyroxenite weathering. As a polyvalent cation, Sc^{3+} is sorbed intensely; its principal sorbents in surface conditions are Fe gels and clay minerals.

If residual brown iron pyrite ores are formed after siderite (Bakal, Akhten, and Ural deposits), scandium concentrations in such ores are usually less than Clarke and amount to 0.0004%. A low content in residual ores ($\leq 0.0005\%$) is due to the lower scandium concentration of the substrate, in this case siderite. When iron ores are melted, scandium passes almost entirely into slag, from which it cannot be extracted [9].

Scandium content in bituminous and brown coal averages 0.0001% [11]. Ash from these coals, however, may contain ≤ 0.0005 –0.04% Sc. Our data indicate that in coal ash of 15 thermoelectric power plants in the USSR contained 0.0003–0.002% Sc. Ash of energy coal, despite a relatively low scandium concentration, is a potential source for extracting it, especially in combination with other metals. Experiments in Canada have shown that Sc, V, Ni, Zn, Sr, and rare earth elements can be extracted from coal ash.

Uranium ores of various types may contain higher amounts of scandium (0.005–0.01%). It has been determined in uranium-rich sandstone (Colorado plateau, USA). Higher concentrations (up to 0.01%) are found in metatuyamunite, hendersonite, and simplotite. A presence of scandium has been discovered in uranium quartzite-like conglomerates in Canada (Blind River) and in South Africa (Witwatersrand), which contain 0.006% Sc and sometimes more. The principal

scandium-concentrating mineral is brannerite (0.05% Sc). Other types of uranium deposits also are promising for scandium [14, 24]. A method of extracting scandium as a byproduct from uranium ore is well developed [15, 16] and has been used in practice in Canada, the United States, and Australia [21].

We have estimated scandium reserves with data on deposits outside of the USSR [3]; this study showed that 90-99% of scandium is to be found in bauxites, titanium ores, and phosphorites. Because of a lack of data, calculations did not include iron or uranium ores. Approximate scandium reserves outside the USSR are considerable, amounting to 1.9 million metric tons. In the future they are likely to be increased from the use of uranium, iron, and some other types of scandium-containing ores. Scandium reserves are substantially higher than those of other rare elements (indium, rhenium, and others). Yet, in terms of production, capitalist and developing nations extract from the earth a small amount of scandium (1700-4900 tons). Most scandium is extracted from bauxites (75-85%) and from ilmenite concentrates and phosphorites (15-20%) (calculated without uranium and iron ores [3]). Aluminum and titanium ores and phosphate material will probably meet most of the increasing industrial demand for scandium. We should remember, though, that scandium production will always depend on the output and processing of ores of the principal useful components (Al, Ti, U, and others), i.e., its output level will closely depend on the production scale of other metals.

* * *

Scandium is a widely scattered element in rocks of the earth's crust and forms no considerable deposits of minerals containing it. However, it occurs frequently in heightened concentrations (<0.02%) in ores in which the main mineral components are iron, titanium, aluminum, uranium, zirconium, phosphorus, and some other elements. Scandium-rich deposits of various genetic types present a possible commercial value: magmatic, contact-metasomatic, greisen-type, hydrothermal, weathering, placer, sedimentary, and metamorphogenic. Largest scandium-containing ore bodies are magmatic titanium and iron deposits, weathering formations, Ti and Zr placers, and sedimentary and metamorphogenic Al, Ti, Fe, U, and P deposits. Scandium reserves in the ores of these deposits can amount to tens of thousands of metric tons. Since the mean scandium content in an ore is usually low (0.002-0.01%), industrial deposits with a large annual ore output hold out the best promise for commercial extraction.

Scandium in extracted ores can accumulate in concentrates of principal minerals (ilmenite, rutile, zircon, etc.), be left in silicate tailings (pyroxenes), or be brought into processing with concentration (bauxites). Ilmenite concentrate usually contains 0.005-0.01% Sc. This content level in concentrate is optimal for producing scandium as a byproduct from titanium material. Bauxites, phosphorites, and uranium ores can be used as scandium sources if they have a content of 0.003-0.01% Sc (rarely more). Zircon concentrate contains up to 0.03-0.1% Sc. Scandium content of ore may vary among titanium, aluminum, zirconium, uranium, and phosphorus deposits, which often reflects their origins. Occurrence areas of principal intrusive rocks that correlate spatially and genetically with endogenous titanium and iron deposits are usually locations of substantial scandium concentration. These scandium-rich deposits were formed mainly during the Precambrian and the Early Paleozoic. The largest deposits were formed in the Archean and Proterozoic times, when large massifs of anorthosites and gabbro-anorthosites were created. During the Middle and Upper Proterozoic, gabbro-anorthosite strata were formed, which are associated with magmatic deposits of scandium-rich ilmenite (the Ukrainian Shield). The Early Paleozoic (Caledonian) was the epoch when large massifs of dunite-pyroxenite-gabbro formations and related titanomagnetite deposits were formed; scandium is mainly concentrated in the pyroxene of these deposits (the Ural).

During the Late Paleozoic and the Mesozoic and Cenozoic, a number of contact-metasomatic, greisen, and hydrothermal deposits developed with a high scandium content. Compared with a group of magmatic deposits of scandium-rich Archean, Proterozoic, and Early Paleozoic ores, however, their role is secondary in terms of scandium production.

Spatially exogenous scandium deposits correlate closely with basite occurrence areas. This should not be surprising, because sedimentary scandium concentrations were formed after decay of older endogenous concentrations. In the territory of the USSR, the largest endogenous scandium accumulations are documented in bauxites formed during the Devonian, Carboniferous, Cretaceous, and Paleogene. Scandium-rich sedimentary (marine and fluvial) iron ores in the USSR are mostly associated with Mesozoic and Cenozoic sediments. Many commercial placers of scandium-rich ilmenite were also formed during the Mesozoic and the Cenozoic; most are prod-

ucts of weathering of basic rocks. Neogene rocks contain accumulations of bone detritus with a higher scandium concentration. Generally, from the Precambrian to the Quaternary the variety of scandium ore concentrations in sedimentary beds increased while the formation of considerable endogenous concentrations slowed down. Exogenous scandium deposits were mainly formed in the Late Paleozoic, Mesozoic, and Cenozoic. Disintegration of rocks of abasic composition played an important role. Scandium-rich residual deposits of titanium, iron, and aluminum exhibit the closest association with basites. Redeposited ores of these metals also often have a higher scandium content.

Of practical interest for extracting scandium as a byproduct are large Al, T, U, P, and Zr deposits; these ores, and especially concentrates, have a higher level of scandium content. Prospecting and exploration should include an assessment of scandium content of all types of ores (see Table 1). The value of an ore is enhanced if stable higher scandium contents can be proved for the ore or the concentrate. Neutron activation analysis is the method of choice in studying scandium prospects of a deposit. Scandium determinations by this method are reliable and can be used to assess proven reserves of scandium.

LITERATURE CITED

1. B. A. Bakhmatov, B. V. Ermolaev, V. A. Ershova, et al., "Trends in the use and development of nuclear physical methods of analysis in geochemical studies," in: *Geochemical Exploration of Rare Metal Deposits* [in Russian], IMGRE, Moscow (1982), pp. 81-87.
2. L. F. Borisenko, *Scandium* [in Russian], Izd-vo Akad. Nauk SSSR, Moscow (1961).
3. L. F. Borisenko, "Scandium resources," *Izv. Vyssh. Uchebn. Zaved. Razvedka*, No. 9, 51-56 (1981).
4. L. F. Borisenko, "Potential value of rare elements contained in ilmenite," in: *Methods of Study of the Technological Properties of Rare Metal Minerals* [in Russian], IMGRE, Moscow (1985), pp. 76-81.
5. L. F. Borisenko, Yu. A. Polkanov, and Yu. P. Sotskov, "Scandium concentrations in placer deposits of ilmenite and zircon," in: *Exogenous Rare Metal Deposits and Methods of Their Investigation* [in Russian], IMGRE, Moscow (1972), pp. 33-39.
6. L. F. Borisenko and V. I. Chudinov, "Distribution of Sc, Ta, Hf, Zr, Co, and Fe in weathering crusts of metalliferous gabbro-norites of Volodarsk-Volyn massif," *Litol. Polezn. Iskop.*, No. 1, 41-48 (1986).
7. L. Ya. Borodin, A. V. Lapin, and A. G. Kharchenkov, *Rare Metal Kamaforites* [in Russian], Nauka, Moscow (1973).
8. E. S. Gutkin, "Geochemistry of scandium in bauxites," *Geokhimiya*, No. 1, 56-64 (1968).
9. L. N. Komissarova, L. F. Borisenko, and V. M. Shatskii, "Feasibility of extracting scandium from pyroxenites," *Zh Prikl. Khim.*, 38, No. 2, 241-244 (1965).
10. *Lateritic Crusts of Weathering of the Kursk Magnetic Anomaly and Their Rare Metal Contents* [in Russian], Nedra, Moscow (1976).
11. L. N. Ovchinnikov and N. A. M. Solodova (editors), *Deposits of Lithophilic Rare Metals* [in Russian], Nedra, Moscow (1980).
12. L. V. Mikhaleva and N. I. Korobova, "Ilmenite sources and placer deposits," *Geol. Geofiz.*, No. 11, 44-50 (1972).
13. V. A. Pchelkin and E. A. Semenova, "National seminar on processing of ores of rare dispersed and radioactive elements (Moscow, May-June, 1978)," *At. Energ.*, 45, No. 6, 462-469 (1978).
14. I. I. Sakhatskii, "Impurity elements in uranium-rich bitumens," *Geokhim. Rudobrazovanie*, No. 7, 43-46 (1978).
15. S. A. Semenov, A. M. Reznik, and L. D. Yurchenko, "Extraction of scandium in complex processing of various raw materials," *Tsvetnye Met.*, No. 12, 43-47 (1983).
16. I. V. Shakhno, Z. N. Shevtsova, P. I. Fedorov, and S. S. Khorovin, "Scandium," in: *Chemistry and Processing of Rare and Distributed Elements* [in Russian], Vol. 2, Vysshaya Shkola, Moscow (1976), pp. 3-45.
17. L. Ya. Shmuraeva, "Mineralogic and geochemical properties of quartz vein wolframite deposits in Primorye," in: *Trace Elements in Minerals* [in Russian], Izd-vo DVNTs Akad. Nauk SSSR, Vladivostok (1976), pp. 82-89.
18. R. Amli, "Carbonatites, a possible source of scandium as indicated by Sc mineralization in the Fen Peralkaline Complex, southern Norway," *Econ. Geol.*, 72, No. 5, 855-859 (1977).
19. C. Frondel, "Scandium-rich minerals from rhyolite in the Thomas Range, Utah," *Am. Mineral.*, 55, No. 5-6, 1058-1060 (1970).

20. R. A. Gulbrandson, "Chemical composition of phosphorites of the Phosphoria formation," *Geochim. Cosmochim. Acta*, 30, 769-778 (1966).
21. F. E. McGinley and J. F. Facer, "Uranium as a byproduct and byproducts of uranium production," in: *Uranium Ore Process*, Vienna (1976), pp. 181-187.
22. D. Nemec, "Scandium in the wolframites of the Bohemian massif and its genetic significance," 36, No. 3, 218-221 (1977).
23. "Scandium extraction process developed," *California Min. J.*, 43, No. 8, 10 (1974).
24. Scandium: Its Occurrence, Chemistry, Physics, Metallurgy, Biology, and Technology, Academic Press, New York (1975).

RARE-EARTH ELEMENTS IN THE FERROMANGANESE NODULES OF THE NORTHERN PACIFIC

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Discussed is the distribution of rare-earth elements (REE) and Y in ferromanganese nodules and the underlying sediments over a Transpacific profile (Japan-Mexico). It is shown that from the continental margins to the Mid Pacific, there is a general trend of increasing accumulation of intermediate REE and Ce in the ferromanganese nodules and the sediments, heavy REE and Y at the lowest concentration levels, and La occupying an intermediate position.

The majority of publications dealing with the geochemistry of the lanthanides and yttrium in the ocean deal with the distribution of these elements in ferromanganese nodules and crusts. Interest in the composition of the ferromanganese formations, including their rare-earth elements (REE), is a function of the potential economic importance of marine ferromanganese nodules as well as of the significance of the lanthanides as indicators. A bibliography of all important publications on REE and Y in marine nodules and crusts is provided in a recent review by A. J. Fleet [24]. Despite the fact that ferromanganese nodules have been studied for some time now, many problems related to the distribution of the lanthanides and Y in them remain. For example, the zoned distribution of the REE and Y in nodules is discussed in [1], the association of the lanthanides and Y with specific mineral phases of the ferromanganese nodules in [23], and the sources of the major components and of the associated REE and Y of nodules and crusts, the mechanism whereby they were incorporated into these formations, the contribution of seawater to the composition of the ferromanganese nodules, etc. in [7, 8, 23, 24]. These last questions are closely related to the problem of the origin of the ferromanganese nodules. Different authors either relate their formation to the sedimentary or diagenetic processes involved in the formation of the sediments, or favor sea-floor hydrothermal activity [12].

In this article we present data acquired in a study of ferromanganese nodules and association sediments on a Transpacific profile (Voyage 46 of the Research Vessel [R/V] *Vityaz'* and Voyage 9 of the R/V *Dmitri Mendeleev*). These data may contribute to solving the questions in dispute we referred to above.

The transoceanic profile (Fig. 1) transects the western and the eastern basins of the North Pacific divided by the Hawaiian Rise. The ferromanganese-nodule fields of the profile are restricted to the abyssal pelagic regions of the ocean. The site coordinates and a detailed geochemical description of the lithology and mineralogy of the host sediments and the ferromanganese nodules of the profile are provided in [8, 10]. As a result of a detailed study of the composition of the bottom sediments, six lithofacies have been identified (cf. Fig. 1) that systematically succeed each other from the continental margins to the pelagic ocean, and it has been proposed that biogenic-terrigenous sedimentation plays the major role in the formation

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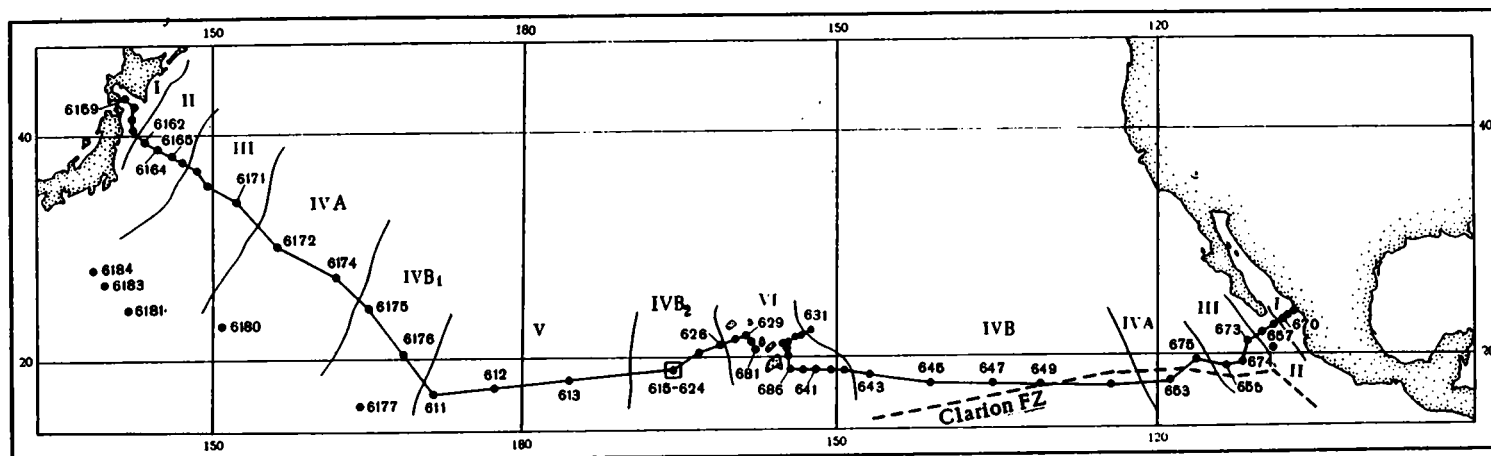


Fig. 1. Transpacific profile: position of stations and lithofacies zones (I-VI).

TABLE 1. Abundances of a Number of Elements in Ferromanganese Nodules (first value), in the Associated Sediments (second value), and in Ferromanganese Crusts (third value)

	Zone	Site no.	Mn	Fe	Ca	Mg	Na	K	P	La	Ce	Sm	Eu	Yb	Lu	ΣREE	Y	Cu	Ni	Co	B	Sr
Western half	IVA	6172	12,5	15,6	0,83	1,82	2,03	1,08	0,18	88	480	27	7,5	13	2	617	—	2580	3 63	1180	390	460
			0,52	0,54	0,9	1,1	2,85	2,6	0,05	29	61	4,5	1,2	3	0,44	99	40	151	182	51	75	170
			0,62	4,42																		
		6174	24,9	15,1	1,25	1,44	1,46	0,75	0,2	120	700	29	7,5	13	2	871	96	5140	8 850	3300	500	670
			—	—	—	—	—	—	—	144	962	32	7,2	11,4	1,55	1158	64	—	—	—	—	335
			0,30	0,35	13,45	1,41	1,66	1,55	0,12	54	93	12,6	4,1	6,5	0,97	171	85	196	196	112	100	560
	V	611	0,39	3,78																		
			14,7	16,7	2,18	1,25	1,08	0,94	0,4	210	1100	45	13	13	1,7	1382	104	1430	2 790	3190	520	870
			22,6	14,4	1,79	1,15	1,44	0,66	0,31	210	1200	45	12	17	1,6	1485	120	3080	4 770	4330	340	990
	612	0,45	0,38																			
0,60		5,51	1,91	1,90	2,30	3,0	0,32	147	308	37	11	13,6	—	522	320	209	210	91	110	300		
17,9		12,8	1,32	1,5	1,51	0,92	0,23	180	830	52	10	15	2,3	1089	112	4480	6 620	2990	290	750		
643	0,45	0,58																				
	0,60	6,4	1,57	2,4	2,2	2,36	—	46	97	12	3,4	5	0,7	164	75	—	—	—	80	180		
	25,3	8,3	—	—	—	—	0,48	139	444	36,6	9,3	14,8	1,4	625	—	9450	12 310	2600	70	—		
649	0,59	0,43																				
	0,77	5,46	0,72	2,43	2,1	2,85	0,11	44	82	9,4	2,8	5,4	0,88	144	64	288	274	113	95	150		
	23,7	9,3	1,79	1,54	1,94	1,03	0,19	120	590	36	11	11	1,5	769	72	7140	12 700	2790	240	590		
653	0,54	0,43																				
	0,76	5,46	0,75	2,44	2,90	2,03	0,17	70	121	13	4,5	—	2	208	96	302	188	100	110	340		
	26,1	8,4	1,68	1,24	2,12	0,9	0,19	120	370	28	5	14	2,2	539	88	8650	11 960	1350	150	580		
675	0,84	0,55																				
	1,5	6,4	1,09	1,64	3,6	2,16	0,16	59	98	16	4,3	6,7	1,1	185	112	509	428	94	84	350		
	18,7	15	—	—	—	—	0,31	41	177	9,6	3,9	4,8	1,2	237	48	3020	6 240	1770	390	—		
655	0,81	0,85																				
	1,21	5,8	1,19	2,1	4,3	2,75	0,16	45	89	11	3	5,1	1	154	88	310	247	99	88	380		

Note. The elemental abundances are given for an untreated dried sample; the values for Mn, Fe, Ca, Mg, Na, K, and P are in %, and those for the other elements in g/ton. The numerator is the content of the reactive Mn and Fe forms in sediments, and the denominator is their bulk content. The data for Fe, Mn, P, Co, Ni, and Cu are taken from [8].

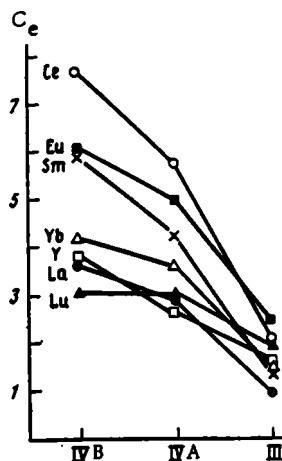


Fig. 2

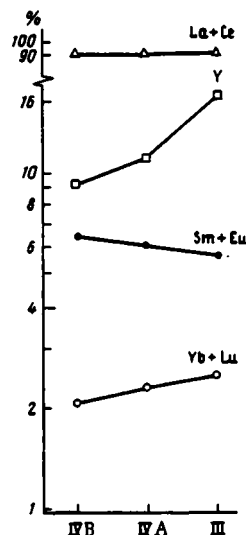


Fig. 3

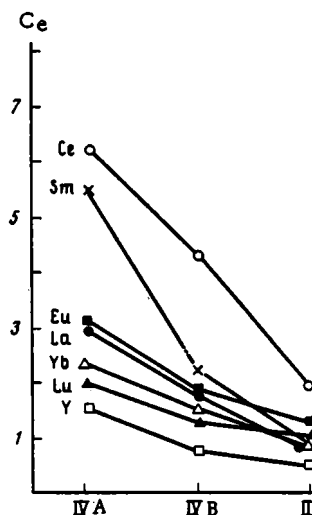


Fig. 4

Fig. 2. Mean shale-normalized abundances of REE and Y in ferromanganese nodules of the eastern half of the profile by zone.

Fig. 3. Evolution in the REE pattern and the role of Y in total FEE + Y of the ferromanganese nodules of the eastern half of the profile.

Fig. 4. Mean enrichment factors C_e of the REE and Y in ferromanganese nodules of the eastern half of the profile relative to associated sediments (by lithofacies zones).

of these sediments [10]. Determination of the Fe + Mn/Ti ratio of the bottom sediments showed that there was no appreciable hydrothermal component present in the surface sediments hosting the ferromanganese nodules, including the sites in the eastern half of the profile (653, 655, 675) in the zone of influence of the Clarion Fracture zone (FZ) (cf. Fig. 1), where mineralogical evidence of hydrothermal activity has been recorded in sediment cores. Except for the ferromanganese nodules from Site 655 on the boundary of the abyssal region of the sea floor, in the zone of transitional-type clays (zone III), all the other ferromanganese formations we studied were taken in the pelagic realm of the ocean, in regions characterized by red clays with volcanic ash (zone IVA) and zeolites (zone IVB), or from carbonate-terrigenous sediments of the submarine seamounts of the Mid Pacific Rise (zone V).

According to data presented in [8], the pelagic nodules metallized throughout contain an average of 36% ore component (as computed from their metal content). The ore minerals, Mn and Fe hydroxides, constitute more than 90% of some ferromanganese nodules. In the nodules we studied, the total Mn and Fe content was generally rather stable (Table 1).

The nonore phases of the pelagic ferromanganese nodules included both allothigenic and authigenic minerals, the same ones found in the underlying sediments [8, 10]. In addition to the rind aluminosilicate grains, volcanic glass is frequently present. Terrigenous clay minerals are common. The authigenic minerals are most frequently represented by zeolites and newly formed minerals belonging to the Fe-smectite group. Phosphatic skeletal debris and fragments of diatom and foram tests are present. In the ore component of the ferromanganese nodules, an x-ray amorphous phase predominates. The weakly recrystallized part of it consists of vernadite, asbolite-buserite and hydrogoethite. Birnessite and todorokite are probably present in the form of very fine grained segregations [8].

The nodules we analyzed were between 0.5 and 3-5 cm in size. The sample included the whole ferromanganese nodule if it was metallized throughout. When a nonmetallic core could be distinctly differentiated, only the metallized rind was sampled. The ferromanganese nodules and the underlying sediments were air dried before being studied.

The REE in the samples were determined by neutron-activation analysis. Data were obtained on the six lanthanide elements La, Ce, Sm, Eu, Yb, and Lu; the precision of the determinations was 10-15%. The samples were analyzed for Y by an x-ray spectroscopic method at a level of analytical error of ~20%. The elements Ca, Sr, Mg, Na, K were also determined by

flame-photometry, and B was determined by a quantitative spectroscopic method. All the analyses were performed in the laboratories of the Institute of the Mineralogy, Geochemistry, and Crystallography of Rare Elements. The REE composition was represented graphically by normalizing the data versus the mean composition of shale lanthanides [27]. The shale-normalized REE and Y abundances were used in constructing the other figures, as indicated in the captions. The correlations between the elements in the ferromanganese nodules and their associated sediments were detected using Spearman's rank correlation and the "shotgun" method, both described in [11], as well as a graphical method.

Distribution of REE and Y in Ferromanganese Nodules. The data acquired allowed us to trace the change in REE and Y abundances for the eastern part of the profile from the zone of continental margin sediments (III) toward mid-ocean (IVB). Figure 2, which was plotted from the information in Table 1, shows the rise in the mean shale-normalized abundances (for each the lithofacies zone) of each lanthanide and Y in the ferromanganese nodules. Only for Lu is this phenomenon not clearly pronounced. A similar tendency in the ratio of the total REE in the ferromanganese nodules was noted for the western half of the transoceanic profile in [7]. As the abundance increases, there is a simultaneous change in the lanthanide pattern. Moving toward the parts of the ocean most distant from the coast, the role of the intermediate REE [IREE] increases, and the importance of the HREE and Y decreases (cf. Fig. 3).

The same tendency is also noted in the distribution of the lanthanides when we examine the enrichment factors C_e of the individual REE and Y in ferromanganese nodules of the eastern part of the profile relative to the associated sediments (cf. Fig. 4). Both the values themselves and their rates of increase proved to be higher for the IREE and Ce than for the HREE and Y, with the value of C_e for Y ordinarily being less than unity. We have previously [4] noted these trends for smaller data sets. The mean C_e values of the lanthanides in the ferromanganese nodules relative to the associated sediments calculated from the information in Table 1 for all the samples analyzed, rank the elements in the following order: Ce (5.4) > Sm (2.8) > Eu (2.4) > La (2.2) > Yb (2.0) > Lu (1.8) > Y (0.74).

A similar fractionation was detected when we compared the mean composition of the REE of the pelagic nodules (calculated as the arithmetic mean of the eight samples in Table 1) to the composition of the lanthanides of the coastal-margin sediments of zone I of the Transpacific Profile [5]. This comparison shows that the REE in the ferromanganese nodules can be ranked according to their C_e values in the following order: Ce (21.1) > Eu (10.5) > Sm (9.5) > La (7.0) > Yb (6.3) > Lu (4.3) > Y (2.8), which is essentially the same as the lanthanide accumulation sequence in the ferromanganese nodules relative to the underlying sediments (except that Eu and Sm trade places). It also has much in common with the ranking of REE according to their enrichment factors in ferromanganese nodules relative to zone I sediments: Eu > Sm > Ce > La > Yb > Y > Lu [5]. In this last case, the difference is in the position of Ce, which occupies the first place in the ferromanganese nodules, surpassing the IREE in efficiency of accumulation, and in the position of Y, which shifts from the penultimate position in the sequence for the pelagic clays to the extreme right-hand side position in the pelagic nodule sequence.

Thus, from the continental margins to mid-ocean one observes a general tendency for the IREE and Ce to be progressively accumulated in both the sediments and the ferromanganese nodules, for the HREE and Y to be present in the lowest concentrations, and for La to occupy an intermediate position.

The similarity of the REE patterns of the ferromanganese nodules and the associated sediments, except for the Ce anomaly of the ferromanganese nodules, can also be seen in Figs. 5 and 6, which show both particular site values and the averaged data. The same appears when comparing the lanthanide patterns of the metalliferous rinds and the nonmetallized cores of the ferromanganese nodules when the core is comprised of the muds underlying the nodule. For example, in a ferromanganese nodule collected at Site 653, the REE content in the outer part is 3-5 times that in the center, while the lanthanide patterns are very similar, if we disregard the Ce maximum of the metalliferous rind (cf. Fig. 5).

The mean REE pattern of the pelagic ferromanganese nodules of the Transpacific Profile is similar to the mean lanthanide pattern of the deep-water nodules as reported by Piper [27] and Ehrlich [22] and to the REE pattern of the iron-rich phase of the ferromanganese nodules described in [23], mirroring the most important features of the lanthanide pattern of abyssal seawater (cf. Fig. 6).

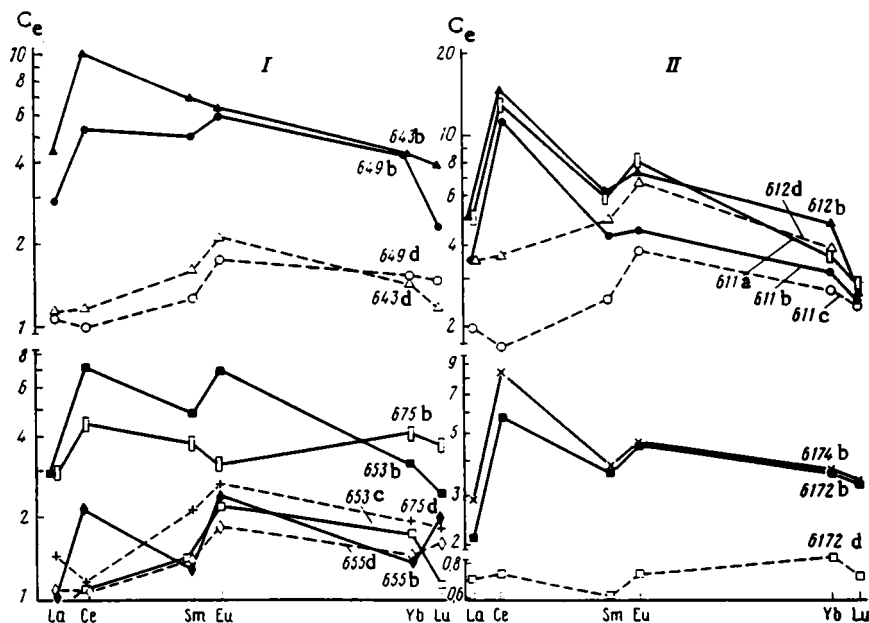


Fig. 5. REE patterns of ferromanganese crusts (a), ferromanganese nodules (b), their cores (c) and associated sediments (d) in the Pacific profile. I - western half of the profile, II - eastern half.

In addition to the ferromanganese nodules proper, one additional sample of ferromanganese crusts developed on fragments of biogenic limestone and basalts (Site 611, in the zone of submarine Mid Pacific seamounts) was analyzed. It was found that the REE pattern and their concentrations in the crusts do not differ substantially from the distribution parameters of the lanthanides in the nodules from the same zone (Sites 611 and 612). It is most important that the ferromanganese nodules and the crusts have similar Fe abundances, while the level of Mn is 1.5 times higher in the nodules (cf. Table 1 and Fig. 5). The ferromanganese crusts that develop on rock exposures and encrust them are hydrothermal (sedimentary) products, according to existing concepts [13]. The similarity of the REE patterns of the ferromanganese nodules and the crusts from zone V is evidence in favor of sedimentary processes also playing a dominant role in the formation of the ferromanganese nodules. The fractionation of the lanthanides in the sediments and the ferromanganese nodules observed on approaching the Mid Pacific is compatible with the very low stability of Ce and the IREE in the aqueous marine environment [1], which is due to their stronger uptake by different sorbing systems and its alteration in sediment. This fractionation reflects the lithofacies zoning of the sediments, the enhanced role of fine fractions and authigenic phases in them, as well as a change in the nature of these against a background of a sharp reduction in sedimentation rates in the same direction [5]. These processes are entirely consistent with the evolution of the seawater REE pattern from the coastal to the pelagic realm and from its surface to its depths [20, 25]. The data we acquired on an actual profile across the ocean do not support the hypothesis of REE zoning in its sediments and Fe-Mn minerals, as developed in [1], and in fact evidence exactly the opposite trends.

Relationship of REE and Y to Other Components of the Ferromanganese Nodules and Crusts.

REE and Y minerals as such have not been detected in marine ferromanganese nodules or crusts by us or by other researchers [24]. In order to detect phases in the nodules including these elements, as well as to shed light on the mechanism whereby they are incorporated, indirect techniques are often employed, chiefly the determination of correlations between them and other components of the ferromanganese nodules. The nonmetallic component of the ferromanganese nodules samples we studied consists, as previously stated, of the same minerals as the underlying sediments. Of especial interest is the abyssal skeletal phosphate, which in a number of cases is markedly higher in REE and Y than are the other minerals [3, 7, 14, 15, 24], but the amount of this phosphate in the nonmetallic component in ferromanganese nodules is normally insignificant [8].

Calculations and plots based on the data of Table 1 showed no strictly linear correlation between the phosphorus and either individual lanthanides and Y or total REE. A tendency to-

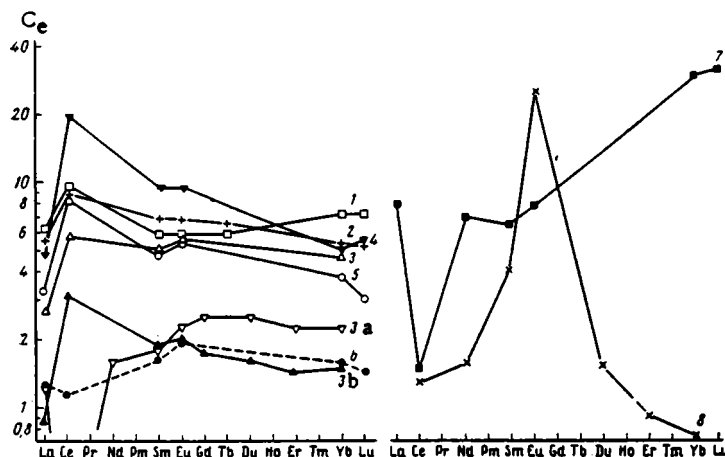


Fig. 6. Mean REE patterns of oceanic ferromanganese nodules and sediments from the data of different authors: 1) shallow-water (<3000 m) and 2) deep-water (>3000-3500 m) marine sediments [27]; 3) ferromanganese nodules from the Equatorial Pacific [23] (3a, P-rich phase of these ferromanganese nodules, 3b, the same, Fe-rich); 4) oceanic ferromanganese nodules from data presented in [22]; 5) ferromanganese nodules (data of the authors); 6) pelagic clays (data of the authors); 7) abyssal seawater $\times 10^8$ [24]; 8) hydrotherms VTP $\cdot 10^4$ [26].

ward such a correlation was observed only for Sm (Table 2). At the same time, all the lanthanides and Y are closely associated with P in the underlying sediments (Table 3). The same relationships between the REE and phosphorus are found in the pelagic and coastal-margin sediments of the entire profile [5]. The good correlation between P and Ce in the ferromanganese nodules and the underlying sediments and in the profile sediments generally should be pointed out in particular. We did not detect the anomalies differentiating Ce from the other REE in the sediments reported in [23]. There is no correlation between the P and Fe abundances in the ferromanganese nodules (cf. Table 2).

The authors made order-of-magnitude estimates of the maximum possible contribution of a P-enriched phase to the total REE abundance in these ferromanganese nodules. In making these estimates it was assumed that all of the P in the nodules (averaging 0.25%) is associated with skeletal debris. In fact, some portion of the P is known to be associated with aluminosilicate minerals, Fe hydroxides, phosphatized grains of biogenic limestone, etc. On the basis of the data presented in [3], the following P and lanthanide element ratios were determined in this material: $P/La = 150$, $P/Ce = 85$, $P/Sm = 180$, $P/Yb = 800$. Using these values and the mean elemental ratios of P and the REE in the pelagic ferromanganese nodules of the Pacific Ocean profile (cf. Table 1) it can be established that skeletal P in these nodules may have associated with it as much as 13% La, 24% Yb, 40% Sm, but only 4.5% Ce. If, however, we take into consideration the extreme numbers obtained for skeletal material by J. Dymond and V. Ek-lund [21] ($P/La = 60$), M. Bernat [15] ($P/Sm = 150$), and J. Arrhenius and E. Bonnatti [14] ($P/Y = 15$), P in ferromanganese nodules may control these elements at levels as high as 31% La, 48% Sm, and 100% Y. These are upper-bound estimates. Thus, the phosphorus-rich phase of the nodules is apparently capable of serving as the carrier of an appreciable, if not the predominant, portion of the REE of the ferromanganese nodules, but only in some cases does it control the abundance of Y. The aforementioned absence of any correlation between the P and REE abundances in the nodules of the profile is consistent with this conclusion.

Other constituents of the nonmetalliferous component of the pelagic ferromanganese nodules that also occur in the underlying sediments, as well as the sediments themselves, exhibit much lower lanthanide abundances than the nodules taken as a whole [5], and therefore clearly cannot play a significant role in the REE balance in the ferromanganese nodules. This is illustrated in particular by the data in Table 1 and Figs. 5 and 6. For example, the pronounced difference in the REE abundance levels between core and metalliferous rind of the nodules from Site 653 previously mentioned can be clearly seen in Fig. 6.

The results of the correlation analysis are in agreement with the description of the non-metalliferous portion of the ferromanganese nodules given above. For elements compositionally

TABLE 2. Correlation Coefficients of the Elements r in Pacific Ocean Ferromanganese Nodules

Elements	r_{calc}	$r_{0.05}$	Elements	r_{calc}	$r_{0.05}$
P-ΣREE	0,42	0,69	Ca-Y	0,07	0,88
P-Sm	0,53	0,69	Mg-ΣREE	-0,6	0,8
P-Y	0,47	0,80	Mg-Y	-0,885	0,878
P-Fe	0,33	0,65	Na-ΣREE	-0,71	0,74
Fe-ΣREE	0,25	0,69	Na-Y	-0,65	0,88
Fe-Ce	0,37	0,69	K-ΣREE	-0,14	0,74
Fe-Y	0,18	0,8	K-Y	-0,54	0,88
Fe/P-ΣREE	0,11	0,65	Sr-ΣREE	1,0	0,69
Mn-ΣREE	-0,23	0,69	Sr-Sm	0,5	0,69
Mn-Y	-0,32	0,8	Sr-Y	1,0	0,8
(Mn + Fe)-ΣREE	0,04	0,69	Sr-Fe	0,6	0,65
(Mn + Fe)-Y	-0,03	0,8	B-ΣREE	0,55	0,65
Mn/Fe-La	0	0,65	B-Y	0,43	0,74
Ca-ΣREE	-0,14	0,74	B-Fe	1,00	0,65

Note. In this table and those that follow r_{calc} is the calculated correlation coefficient; $r_{0.05}$ is the correlation coefficient allowed at the 95% confidence level.

associated primarily with the nonmetalliferous component of the nodules, such as Mg and Na, an inverse relationship is noted with the REE and Y, and with Ca and K there is no correlation (cf. Table 2).

Based on the foregoing one can conclude that the nonmetalliferous phase of the ferromanganese nodules samples studied serves to dilute the REE abundances in nodules, and that the major portion of the REE must be associated with the metalliferous component. However, no linear correlation was observed between its major constituents (Mn and Fe) and either the individual lanthanides and Y, or the total REE (cf. Table 2). Nor is there any correlation between total Mn + Fe, the Mn/Fe and Fe/P ratios and REE and Y abundances in the nodules or their underlying sediments (cf. Tables 2 and 3). If we eliminate the ferromanganese nodules of Sites 655 and 6172 located at boundaries of the pelagic realm, when we compute the correlation coefficients, we obtain a linear relationship between the Fe and Ce abundances and between the Fe abundance and total REE. These results are in good agreement with the association between Fe and ΣREE observed by Volkov and Fomina in pelagic ferromanganese nodules

from the western part of the profile [7]. But for La, Sm, Yb, and Y there is no correlation in any region. As a result of the inverse nature of the relationship found between the Fe and Mn abundances in the nodules when the sites referred to above are eliminated (cf. Table 1), a corresponding tendency to an inverse correlation between Mn and total REE, individual lanthanides, and Y is manifested, but a strictly linear dependence was not detected in the sediments underlying the ferromanganese nodules, however, a tendency is noted toward a direct relationship between the bulk Mn abundances and REE and Y abundances (cf. Table 3).

At the same time, a positive linear correlation of Ce and other REE with Fe and an inverse relationship with Mn/Fe is noted in [23] for essentially "todorokite" abyssal (>4000 m) ferromanganese nodules from the Equatorial Pacific. In the sediments underlying these nodules no correlation between Ce and the bulk Fe abundance was found, as in our data (cf. Table 3), but for the other REE a direct correlation was found with the ratio of the bulk Mn and Fe abundances. At the same time the authors of [23] report the existence of a relationship between all of the lanthanides except Ce and the phosphorus content in the ferromanganese nodules and associated sediments. There is no relationship between Ce and P, according to their data, and the nodules with elevated total REE abundances are characterized by a higher Fe/P ratio. These observations are in agreement with the results we obtained in an experiment on leaching a nodule with 0.1 M HCl, which showed that while practically no Fe and Mn go into solution, 66% of the P does, and roughly 64% of the trivalent REE. Only a small amount (6.7%) of the Ce is removed along with the phosphorus. Elderfield et al. [23] interpret these relationships among the ferromanganese nodules constituents and the experimental results as evidence for the abundances and patterns of REE in "todorokite" nodules being controlled by two phases: 1) one enriched in Fe with an REE pattern that mirrors that of seawater lan-

TABLE 3. Correlation Coefficients of the Elements in Sediments of the Pacific Profile Underlying Ferromanganese Nodules

Elements	r_{calc}	$r_{0.05}$	Elements	r_{calc}	$r_{0.05}$
P—La	1,0	0,69	Fe _{bulk} —Y	0,25	0,59
P—Ce	1,0	0,69	Mn _{bulk} —ΣREE	0,60	0,62
P—Eu	1,0	0,69	Mn _{bulk} —Y	0,60	0,62
P—Yb	1,0	0,69	(Fe _{react} + Mn _{react})—ΣREE	0,42	0,69
P—Y	0,93	0,65	(Fe _{react} + Mn _{react})—Y	0,52	0,74
P—Fe _{bulk}	-0,14	0,74	Mn _{bulk} /Fe _{bulk} —La	-0,125	0,69
Fe _{bulk} —ΣREE	0,11	0,56	Fe _{react} /Mn _{react} —ΣREE	0,5	0,69
Fe _{bulk} —ΣREE	0,25	0,69			

thanides (cf. Fig. 6); and 2) one enriched in P, with the skeletal debris REE pattern. Elderfield et al., however, emphasize the difference in principal between the distribution of Ce and the behavior of the other REE.

However, the REE data of the nodules and associated sediments we obtained differ in many respects from the results reported in [23] (cf. Tables 2 and 3), and are more consistent with those of Calvert and Price [16], who did not find any correlation between Fe and Ce abundances in the Pacific Ocean pelagic nodules, in which the manganese phase is generally an x-ray amorphous substance and weakly recrystallized vernadite (as in the nodules we studied). In ferromanganese nodules of this type there is also no correlation between P and the REE.

It should be noted in particular that there is a direct linear relationship between the abundances of Sr and of the ΣREE, Ce, La, and Y for the nodules of the profile. At the same time, no correlation was found for Sr and IREE (Sm) with the HREE (Yb) (cf. Table 2). The presence of a common factor can be assumed that determines the abundance of the LREE, as well as the total REE and Sr in the nodules.

There is no correlation between Ca and the REE in the ferromanganese nodules studied, as already noted. Nor has any been detected for the Ca—Sr pair. The Ca/Sr ratio (18-32) and the Ca/ΣREE ratio (12-31) in the nodules are much smaller than in biogenic marine limestones (Ca/Sr = 150-700, Ca/ΣREE = $1 \cdot 10^5$) and in phosphates (Ca/Sr = 75-150, Ca/ΣREE = 75-150) [2, 6, 23, 29]. Apparently the abundances of REE and Sr are not controlled by contamination from these sources in ferromanganese nodules. At the same time, a tendency to a positive correlation is observed between the Sr and Fe abundances in the nodules (cf. Table 2), and a negative correlation for Sr and Mn. These data speak in favor of the preferential association of Sr, and thus, of the ΣREE, with the iron-oxide phase of the ferromanganese nodules.

A trend is also observed in the nodules for a positive correlation of the ΣREE, as well as Ce and La, with boron, although a strictly linear dependence was not found (cf. Table 2). Boron is closely associated with Fe in the ferromanganese nodules (cf. Table 2). The tendency for the abundances of boron and the REE to be related in nodules is one more factor in favor of the lanthanides in ferromanganese nodules being controlled primarily by a Fe phase.

Thus, the results of our work support in large measure the hypothesis that the REE in pelagic ferromanganese nodules (the manganese phase of which is an x-ray amorphous substance with weakly recrystallized vernadite and asbolite-buserite being present) are primarily associated with the iron component of the nodules. Most closely associated with this component are the LREE that determine the total abundances of the lanthanides (Ce in particular and La to a lesser extent). The abundances of the intermediate and the heavy REE and Y are much more weakly constrained, and for these elements it is possible that there is an appreciable contribution from a phosphorus-enriched phase, presumably fishbone apatite. The absence of a linear relationship between the lanthanides and Y in the ferromanganese nodules, on the one hand, and bulk Fe on the other, is probably due to the fact that the REE and Y are selectively associated only with specific varieties of the Fe oxides in the ferromanganese nodules.

Relationship between the Lanthanides of the Ferromanganese Nodules and Those of the Underlying Sediments. The relationship between the metallic constituents of the ferromanganese

TABLE 4. Correlations between Abundances of the Same Elements in Ferromanganese Nodules and the Associated Sediments

Elements	r_{calc}	$r_{0.05}$	Elements	r_{calc}	$r_{0.05}$
ΣREE	0,69	0,74	$\Sigma \text{REE} / \text{Mn}_{\text{react}} + \text{Fe}_{\text{react}}$	0,86	0,80
La	0,78	0,74	Fe _{bulk}	0,43	0,74
Ce	0,67	0,74	Fe _{react}	0,43	0,74
Sm	0,33	0,69	Mn _{bulk}	0,43	0,74
Yb	0,09	0,69	Mn _{react}	0,43	0,74
Y	0,26	0,80	Mn _{bulk} / Fe _{bulk}	0,14	0,74
$\Sigma \text{REE} / \text{Mn}_{\text{react}}$	0,65	0,80	Mn _{react} / Fe _{react}	0,79	0,80
$\Sigma \text{REE} / \text{Fe}_{\text{react}}$	0,75	0,80	P	-0,14	0,74

nodules and the associated sediments is regarded as supporting the hypothesis of the diagenetic nature of the nodules [8, 23]. For example, Elderfield et al. [23], basing their arguments on bulk abundances, note an inverse correlation between the REE (except Ce) in essentially "todorokite" nodules and associated sediments in all seven samples taken in a 230 km² study area in the abyssal Equatorial Pacific. In contrast to the other lanthanides, Ce, which can occur as a tetravalent form, exhibits a tendency to direct correlation. The authors consider the existence of an inverse linear relationship for the majority of the REE to be evidence of their diagenetic nature in ferromanganese nodules, while Ce, in their view, was incorporated into the nodules directly from seawater and was not involved in diagenetic processes. It is difficult to imagine, however, such a radical fractionation of the lanthanides, this most closely related and geochemically coherent group of elements. There is abundant evidence attesting to their excellent correlation.

However, statistical treatment of our data showed (Table 4) that there is no strictly linear dependence between the bulk abundances of total REE in the ferromanganese nodules and the associated sediments studied. Only a tendency toward a positive correlation is detected. This is supported in particular by the fact that, in contrast to Elderfield et al. [23], we found a weak direct relationship between the La abundances of nodules and sediments. For the other REE and Y, similar relationships between bulk abundances were not detected. The calculated correlation coefficients for the HREE and Y are exceptionally low (cf. Table 4). The lack of a correlation between the REE patterns in the ferromanganese nodules and in the associated sediments has been noted for the Western Pacific [7].

The tendency toward a positive relationship between the bulk abundance of total REE in the nodules and associated sediments we studied has also been found by comparing the quantities $\text{REE} / \text{Mn}_{\text{react}}$, $\Sigma \text{REE} / \text{Fe}_{\text{react}}$, and $\Sigma \text{REE} / \text{Mn}_{\text{react}} + \text{Fe}_{\text{react}}$. Although no strong relationship was found, a clear trend toward a direct relationship was found for $\Sigma \text{REE} / \text{Fe}_{\text{react}}$, and a weak linear relationship was discovered for $\Sigma \text{REE} / \text{Mn}_{\text{react}} + \text{Fe}_{\text{react}}$ (cf. Table 4). Similar relationships were also established for $\text{La} / \text{Mn}_{\text{react}} + \text{Fe}_{\text{react}}$ and $\text{Ce} / \text{Mn}_{\text{react}} + \text{Fe}_{\text{react}}$.

A more reliable test of the hypothesis that ferromanganese nodules are diagenetic in origin could be made by comparing the elemental abundances in the nodules with their abundances in the associated sediments for the reactive (rather than bulk) forms. But for elements of the so-called manganese ferromanganese nodules and sediments, among which Volkov et al. [8] also include the REE, the quantitative characteristics of the bulk and reactive forms in the underlying sediments are fairly close in many cases. As a result, they consider it permissible to compare the bulk abundances of these elements [8].

Analysis of the correlations between the reactive forms of Fe and Mn (double extraction [acid and reducing agent] of Chester and Hughes [17]) and the correlations between their bulk abundances in sediments and the abundances of these elements in the ferromanganese nodules we studied reveal no close associations between them. The bulk Mn/Fe ratios in the ferromanganese nodules and in the associated sediments are also not correlated. But for the reactive forms such a tendency is observed. There is also no relationship found between the bulk phosphorus contents (cf. Table 4).

Volkov et al. [8], on the basis of data for a Pacific profile, arrived at a conclusion contrary to those presented in [23]. These researchers see proof of a diagenetic origin of the ferromanganese nodules in the correlation between the enrichment factors of the major metal components and the trace elements in the ferromanganese nodules and the underlying sediments. In other words, the trace-element abundance in the nodules is determined, in their opinion, by the abundance of these elements in the sediments underlying the ferromanganese nodules. It should be pointed out, however, that the existence of a linear relationship between elemental abundances or their ratios in the ferromanganese nodules and the sediments is not unambiguous evidence of an inherited relationship. It is quite possible that the enrichment in the nodules and the associated sediments is constrained by the same external factors operating concurrently and in the same direction.

Thus, our data do not reveal a close correlation between the composition of the pelagic ferromanganese nodules of the Pacific Ocean profile and the associated sediments, and are not entirely consistent with an important criterion for the dominant role of diagenesis in the formation of these nodules.

* * *

On the basis of a study of the mineralogical and chemical composition of ferromanganese crusts, nodules, and the fine-grained phase of sediments in the Line Island Archipelago region of the Pacific, Aplin and Cronan [13] have clearly formulated the existing ideas about the purely sedimentary (hydrogenous) formation of crusts and their sedimentary or diagenetic accretion during the genesis of ferromanganese nodules. For example, the formation of nodules consisting mainly of an x-ray amorphous metallic substance, according to their data, involved both types of accretion, and the metal components entered them both directly from the water column and from the associated sediments. They are a product intermediate between crusts and the ferromanganese hydroxides of the bottom sediments. A biogenic supply of metals to the surface of marine sediments may qualitatively explain the difference between the chemical composition of the ferromanganese nodules and the Fe-Mn oxides in the sediments. "Todorokite" ferromanganese nodules are diagenetic, and the "todorokite" precipitated from pore waters. These ferromanganese nodules are restricted to regions of surface waters of relatively high biological productivity, thereby underscoring the important role played by biogenic material in their formation, as scavenger and as transmitter of metals and C_{org} to the sea floor.

Our data on the correlations between the different components in the pelagic ferromanganese nodules and associated sediments, and the ratios of the REE to other elements in these formations, are not inconsistent with the foregoing outline of the formation of nodules consisting mainly of an x-ray amorphous metalliferous substance or with the hypothesis of the preferential association of lanthanides with the Fe-oxide phases of ferromanganese nodules.

It is known that most researchers favor seawater as the original source of the lanthanides and Y in ferromanganese nodules [24]. The REE pattern of pelagic nodules mirrors that of seawater and apparently formed as a result of the preferential uptake of Ce and the LREE from it due to their better sorbing characteristics [1]. This hypothesis regarding the original source is supported by the value of the $^{143}Nd/^{144}Nd$ isotopic ratio of 0.51244 found by Elderfield et al. [23] in ferromanganese nodules, a value close to its value in seawater. However, similar values for this ratio were also found by these same workers for the associated sediments. Thus, even though seawater is the most probable source of the lanthanides, the mechanism whereby the REE pattern of the pelagic ferromanganese nodules developed remains obscure. There is no precise idea about the contributions of seawater, pore waters, and the fine-grained Fe-Mn phase of the underlying sediments to the lanthanide mass balance [24]. Seawater is also regarded as the major supplier of REE for hydrothermal Fe-Mn minerals in the ocean [1, 9, 28], but the lanthanide patterns of hydrothermal minerals differ from the REE patterns of pelagic ferromanganese nodules. Dubinin et al. [9], following ideas once expressed by N. M. Strakhov, see the main cause for these differences in a much slower rate of ferromanganese nodules formation compared to the rate of formation of hydrothermal deposits. As a result, the Fe and Mn hydroxides of the hydrothermal formations absorb REE from seawater without fractionation, unlike the hydroxides forming ferromanganese nodules.

The rapidity with which hydrothermalites form, the relatively high (to tenths of a percent) abundances of REE in them, and the exceptionally low concentration of lanthanides in seawater ($\sum REE \sim 1 \cdot 10^{-9} \%$ [20, 25]) make the rapid concentration of REE (by a factor of 10^8) necessary if seawater is to be considered as essentially the sole source of the lanthanides

in hydrothermalites [9]. Such concentration is difficult to achieve. There are grounds for believing that another source in addition to seawater may be the hydrotherms themselves. Information about the REE abundances and patterns in hydrotherms on the sea floor remains ambiguous [26], and it is quite likely that these parameters vary depending on the physicochemical conditions of the hydrothermal systems in oceanic basalts. There is no doubt, however, that their REE abundances are several orders of magnitude higher than in seawater, and this may allow for the rapid concentration of the lanthanides on ferromanganic hydroxides even before these come into contact with the bottom water. One piece of evidence supporting the possibility of this process occurring is the europium maximum that appears to be characteristic of sea-floor hydrotherms [26] and which has been detected in the REE patterns of Fe-Mn minerals in Galapagos Rift hydrothermal mounds [18] and the Atlantis II depression of the Red Sea [19].

In contrast to the Mn-Fe hydrothermal minerals, the protracted formation of pelagic ferromanganese nodules allows for significant concentration and fractionation of the lanthanides even from a source as poor as seawater, helped in no small measure by biogenic material scavenger and transmitter of metals to the sea floor. These factors apparently are responsible for the uniqueness of the REE patterns of the Fe-Mn formation of different origins.

In conclusion it should be emphasized once again that the fractionation of REE is most distinctly manifested in the pelagic realm, as shown by the fact that the HREE, which are most stable in aqueous solution, play a more important role in seawater, and Ce and the IREE, which are least mobile in a marine environment, to a great extent come out of solution and enter the sediment as a result of being scavenged by different sorbing systems. This was noted earlier [4], in a general way, for all REE hydrolyzates. As a result of fractionation in ferromanganese nodules and associated sediments of the pelagic realm, which is characterized by exceptionally slow sedimentation rates and the important role played by authigenic minerals in the sediments, the REE patterns are enriched in Ce and the IREE, and in the actual profile from the continental margins to mid-ocean, a tendency is observed for the portion of IREE and Ce to increase, and for the role of HREE and Y to decrease in the lanthanides of the bottom sediments and in ferromanganese nodules.

LITERATURE CITED

1. Yu. A. Balashov, *Geochemistry of the Rare Earth Elements* [in Russian], Nauka, Moscow (1976).
2. G. N. Baturin, *Sea-floor Phosphorites* [in Russian], Nauka, Moscow (1978).
3. A. M. Blokh and A. V. Kochenov, "Contaminant elements in the skeletal phosphate of fossil fish," in: *Geology of Rare-Earth-Element Deposits* [in Russian], Vol. 24, Nedra, Moscow (1964), p. 83.
4. T. F. Boiko, N. A. Lisitsyna, G. Yu. Butuzova, et al., "Rare-element hydrolyzates in sediments over a Pacific-Ocean profile," *Litol. Polezn. Iskop.*, No. 3, 19-30 (1979).
5. T. F. Boiko, N. A. Lisitsyna, and G. Yu. Butuzova, "Rare-earth elements and lithofacies zoning of marine sediments (Transpacific profile). Communication 1," *Litol. Polezn. Iskop.*, No. 3, 3-13 (1988).
6. V. V. Burkov and E. K. Podporina, *Strontium. Mineralogy, Geochemistry and Major Deposit Types* [in Russian], Izd. Akad. Nauk SSSR (1962).
7. I. I. Volkov and L. S. Fomina, "New data on the geochemistry of rare-earth elements in Pacific sediments," *Geokhimiya*, No. 11, 1603-1615 (1973).
8. I. I. Volkov, L. E. Shterenberg, and L. S. Fomina, in: *Ferromanganese Nodules: Diagenetic Geochemistry of Pacific Ocean Sediments (Transoceanic Profile)* [in Russian], Nauka, Moscow (1979), pp. 169-223.
9. A. V. Dubinin and I. I. Volkov, "Rare-earth elements in the metalliferous sediments of the East Pacific Rise," *Geokhimiya*, No. 5, 645-661 (1986).
10. *Lithology and Geochemistry of Pacific Ocean Sediments (Transoceanic Profile)* [in Russian], Nauka, Moscow (1979).
11. R. L. Miller and J. S. Kahn, *Statistical Analysis in the Geological Sciences*, Wiley, New York (1962).
12. N. M. Strakhov, *Problems in the Geochemistry of Modern Oceanic Lithogenesis* [in Russian], Nauka, Moscow (1976).
13. A. C. Aplin and D. S. Cronan, "Fe-Mn oxide deposits from the Central Pacific Ocean. I - Encrustites from the Line Islands Archipelago. II - Nodules and associated sediments," *Geochim. Cosmochim. Acta*, 49, No. 2, 427-451 (1985).

14. J. Arrhenius and E. Bonatti, "Neptunism and volcanism in the ocean," in: *Progress in Oceanography*, Vol. 3, Pergamon Press, New York (1965), pp. 7-22.
15. M. Bernat, Les isotopes de l'uranium et du thorium et les terres rares dans l'environnement marin, *Cah. ORSTOM, Ser. Geol.*, 7, 65-85 (1975).
16. S. E. Calvert and N. B. Price, Geochemical variation in ferromanganese nodules and associated sediments from the Pacific Ocean, *Mar. Chem.*, 5, 43-74 (1977).
17. R. Chester and M. I. Hughes, "A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments," *Chem. Geol.*, 2, No. 3, 249-262 (1967).
18. J. B. Corliss, M. Lyle, J. Dymond, and K. Crane, "The chemistry of hydrothermal mounds near the Galapagos Rift," *Earth Planet. Sci. Lett.*, 40, 12-24 (1978).
19. C. Courtois and M. Treuil, "Distribution des terres rares et de quelques éléments en trace dans les sédiments récents des fosses de la Mer rouge," *Chem. Geol.*, 20, 57-72 (1977).
20. H. J. W. De Baar, M. P. Bacon, P. G. Brever, and K. W. Bruland, "Rare earth elements in the Pacific and Atlantic oceans," *Geochim. Cosmochim. Acta*, 49, No. 9, 1943-1960 (1985).
21. J. Dymond and W. Eklund, "A microprobe study of metalliferous sediment components," *Earth Planet. Sci. Lett.*, 40, 243-251 (1978).
22. A. M. Ehrlich, "Rare-earth abundances in manganese nodules," Ph. D. Thesis, MIT (1968).
23. H. Elderfield, C. J. Hawkesworth, M. J. Greaves, and S. E. Calvert, "Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments," *Geochim. Cosmochim. Acta*, 45, No. 4, 513-526 (1981).
24. A. J. Fleet, "Aqueous and sedimentary geochemistry of the rare earth elements," in: *Rare Earth Element Geochemistry*, P. Henderson (ed.), Elsevier, Amsterdam-Oxford-New York-Tokyo (1984), pp. 343-374.
25. O. T. Hogdahl, S. Melsom, V. T. Bowen, "Neutron activation analysis of lanthanide elements in sea water," in: *Advances in Chemistry Series*, Vol. 73, pp. 308-325 (1968).
26. A. Michard, "The REE content of some hydrothermal fluids," *Chem. Geol.*, 55, No. 1-2, pp. 51-60 (1986).
27. D. Z. Piper, "Rare earth elements in the sedimentary cycle: a summary," *Chem. Geol.*, 14, No. 4, 285-304 (1974).
28. D. Z. Piper and P. A. Graef, "Gold and rare earth elements in sediments from the East Pacific Rise," *Marine Geol.*, 17, No. 5, 287-297 (1974).
29. K. K. Turekian and K. H. Wedepohl, "Distribution of the elements in some major units of the earth's crust," *Bull. Geol. Soc. Am.*, 72, No. 2, 175-191 (1961).

Five facies zones are distinguished in upper Permian marine deposits of Novaya Zemlya and the northern part of the Timano-Pechorsk region. We draw a conclusion of basic similarity between the terrigenous sediment accumulation in the Permian geosyncline of Novaya Zemlya and the contemporary ocean. .

Paleozoic geosynclinal deposits in general, and their edges in particular, are generally complexly disturbed, often overthrust and pierced by intrusions. Because of this, in order to determine the sequence and width of the facies zones, we were obliged to have recourse to palinspastic reconstructions, which naturally reduces the reliability of the structures.

Novaya Zemlya is one of several regions where the Paleozoic geosynclinal complex is a direct extension of the Ural geosyncline [10] stripped of granitoid magmatism. In distinction from the Urals, Hercynian folding is not apparent on Novaya Zemlya. In connection with this, Permian deposits enter the composition of the geosynclinal complex, but not the frontal downwarp as in Urals. Only at the end of the Triassic-start of Jurassic did a series of large scale, relatively simply constructed anticlinoria and synclinoria form here. On Yuzhnaya island they are complicated by a series of finer steep folds and fractures. Large scale thrust faults don't exist in the region, and therefore the sequence and width of the facies zones may be determined without palinspastic construction.

The general characteristics of the region and facies zonality are presented in a series of articles [5, 9, 10]. The present article is devoted to the detailed characteristics of facies zonality in deposits of the second half of Ufimian time in the late Permian. In the south of Novaya Zemlya these deposits are distinguished by the name of the Belushkinsk suite [5], while more to the north they are called the Karmakul'sk series [7]. In the Pechorsk basin, the lower part of the Pechorsk series corresponds to this stratigraphic interval, and in the Timano-Pechorsk region it corresponds to the Ekushansk suite [2, 4].

The conclusion of the age interval is indicated by the fact that at this time in the Paleozoic Novaya Zemlyan geosynclinal basin a huge quantity of terrigenous material begins to be carried out from the eroding folded Hercynian structure of the Uralides [6, 8]; before this, all of the terrigenous material was deposited within the limits of the Pre-Ural downwarp. In connection with this, the chemogenic-organogenic sediment accumulation which was more predominant earlier on Novaya Zemlya yielded to terrigenous and facies zonality determined by the dynamics of terrigenous material. The younger Kazansk-Tartaris deposits in the eastern part of Severnyi island are eroded. Thus, the considered interval is unique in that terrigenous sediments were preserved in every facies zone, from the shelf to the basin floor.

The factual material forming the basis of this article was mainly collected by L. G. Povysheva during geologic surveying and thematic efforts from 1974 to 1985. Determination of the brachiopods, on which correlation of the sections in the southern part of region is based to a significant degree, was performed by V. I. Ustritskii. All available data was used during the work from geologists of the western Arctic party PGO "Sevmorgeologiya," E. G. Platonova, V. V. Orgo, G. V. Trufanova, V. D. Nepomilueva, et al. Material on Permian deposits of Kolguev island and the Timano-Pechorsk region is adapted from [2, 4]. This made it possible to construct a facies profile intersecting all of the facies zones (Fig. 1, 2), from the continent to the floor of the geosynclinal basin inclusively, and to give their detailed characteristics; primary consideration is given to deposits of the basin slope and floor. As seen from the presented figure, the profile traverses a meridian direction, including the northern part of the Timano-Pechorsk region, Kolguev island and a large part of Novaya Zemlya. Its total length is more than 700 km.

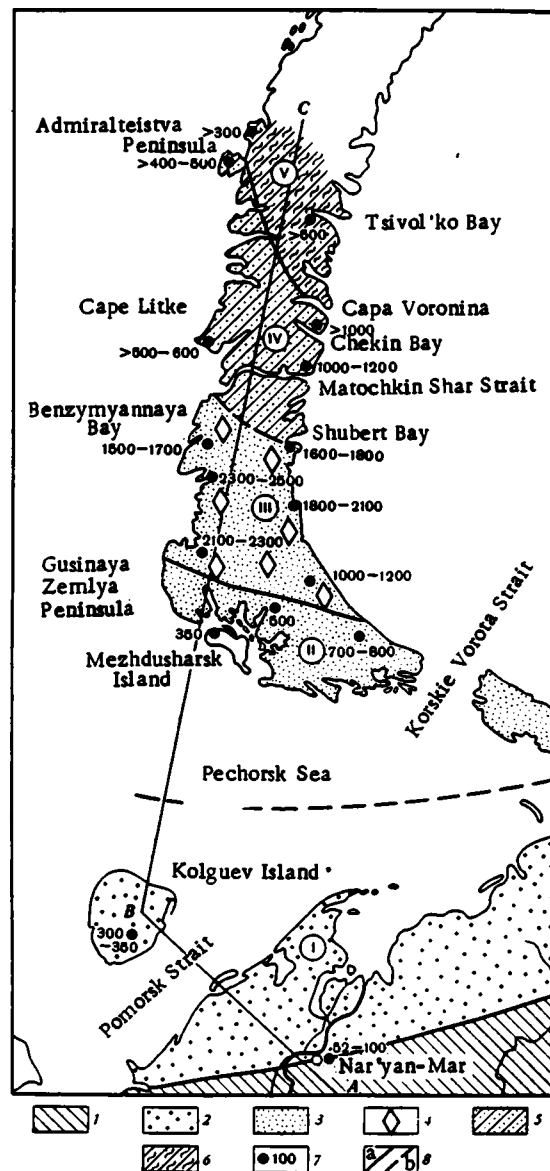


Fig. 1. Position of the facies profile, mapped in Fig. 2: 1) coastal plain; 2) shelf; 3) continental slope; 4) foot of the slope, wild-flysch zone; 5) basin floor, sand turbidite zone; 6) basin floor, clay turbidite zone; 7) section sites and deposit thicknesses, m; 8) boundaries of facies zones [a) established, b) proposed]. Roman numerals refer to facies zones.

As is known [2, 3], in the Ufimian stage of the late Permian, continental deposits developed in the southern greater part of the Timano-Pechorsk region. More to the north, approximately at the latitude of the town of Nar'yan-Mar, they begin to be replaced by marine deposits, in the composition of which are distinguished five facies zones.

The first zone, nearly 250 km wide, encompasses the northern part of the Timano-Pechorsk region and Kolguev island. The position of its northern boundary in the sea is not completely clear. Judging by materials from Vaigach island and the southern termination of Novaya Zemlya, it occurs at the latitude of Yugorskii Shar strait. Thin shallow water (marine) clay-sand sediments of the Ekushansk suite [3], containing rich complexes of benthic fauna, accumulated here in Ufimian time. The transition from the coal-bearing parallel deposits of the southern part of the Timano-Pechorsk region to the marine sediments of Kolguev island is accompanied by a gradual increase of thickness. If it reaches several tens of meters in the southern part of the zone (72 m in a stratotypical section of a well at Nar'yan-Mar), then on Kolguev island it reaches 350 m.

The second zone has a width of nearly 150 km, and occupies all of the southern part of Yuzhnaya island of Novaya Zemlya. Its northern boundary occurs on the line between the Savina river basin and the middle of the Gusinaya Zemlya peninsula. The Belushkinsk suite developed here is divided on the east into two subsuites: the lower, with a thickness of 200-300 m, essentially sandstone, and the upper, with a thickness of 450-500 m, represented by rough alternation of packets of sandstones and argillites with single interlayers of chlidolites, in which separate limestone olistoliths of Devonian and early Carboniferous age are present. The size of the olistoliths ranges from several centimeters to 7 m in cross section.

The sandstones are, as a rule, unlayered and formed in massive beds. Signs of sediment creep are observed on the bedding surfaces: cylinders, mounds, and erosion channels. Sandstone beds overflowing with clay pellets are characteristic. The sandstone composition is polymict, close to greywacke. Terrigenous material is poorly rounded, weakly sorted. The cement is clay (of hydromica and chlorite-hydromica composition), often with an admixture of weakly dispersed scraps of carbonified plant tissues. The quantity of cement reaches 15-20%. An insignificant admixture of carbonate in the cement exists only in the very southern sections. Here, in the southern part of the zone, also occur sparse interlayers containing rich benthic fauna; to the north only single gastropods and pelecypods are encountered. Allocthonous remnants of flora are very general, sometimes completely definable. The thickness of the deposits varies from 350 m in the southwest of the zone to 700-800 m in its northwestern part. Judging by the presence of olistoliths of Devonian and Carboniferous rocks which also occur higher in the section, in places in the southern part of the zone Ufimian sediments are generally absent (apparently, this interval occurs in the Pechorsk Sea). This zone, judging by numerous signs of sediment flow, represents slope deposits.

The third zone has a width of 130-150 km. Its northern boundary occurs on the west of the archipelago between the Bezymyannaya and Mityushikhaya inlets, and on the east in the region of Shubert bay. A characteristic of the zone is the sharp increase of thickness (up to 2100-2500 m) and the complication of the section of the Belushkinsk suite. Here it is subdivided into three subsuites with thicknesses from 700-900 m.

The lowest subsuite is made of massive sandstones with two thick (up to 100 m) packet of olistostromes. The middle subsuite contains the greatest quantity of olistostromes; sorted rocks are present in a lesser quantity. The upper subsuite is represented by platy sandstones interlayered with argillites and olistostromes.

The most characteristic rocks of this zone are the olistostromes described in detail [7] in the region of Pukhovaya bay. Clay, silt, and sand material in the olistostromes form a matrix, including randomly distributed olistoliths ranging in size from a few centimeters to several meters. The olistolith composition is distinct. They are most often represented by terrigenous rocks of Permian age and less often by limestones of Carboniferous and Devonian age. The quantity of fragments and lumps in olistostromes is variable, from single examples to conglomeratelike rocks. Many olistoliths represent fragments of layers and packets of terrigenous Permian rocks, sometimes in the form of layers or blocks with preserved layering, often intricately deformed, corrugated, forming various loaf or spiral shaped structures and twists. It is possible to observe initially horizontal layering that has been completely re-crumpled in many olistoliths. Plastic deformation textures are sometimes noted even in thin sections. The bodies of olistostromes are lenticular and traceable along strike for tens and hundreds of meters, seldom kilometers; the thickness of the bodies reaches a few tens of meters, but sometimes in bulges it also reaches 100 m. The absence of sorting and orientation of large-scale plastic olistoliths, which are often arranged perpendicular or inclined to the lower surface of the olistostromal layer, indicates that the latter represents viscous sludge flows, creeping downwards on the slope of the basin. This is also indicated by the character of the lower boundary of olistostromal flows: it is uneven, with sharp pockets and tongue-like intrusions into underlying rocks, which are apparently a consequence of the active erosion of these deposits by moving flows.

Faunal remnants in the deposits of this zone are sparse and divided into three groups by burial conditions: a) sparse foraminifera and radiolaria, preserved in concretions and buried, apparently in situ; b) single large scale brachiopods and pelecypods, as a rule, deformed and broken, which crept on the basin slope together with sediment; c) fauna included in boulders and pebbles as well as redeposited. The first two groups were buried more or less at one age and are synchronous with the sediment, that is, they are characteristic of the base of the upper Permian. The third group has an age range from the end of the Devonian to early Permian. Remnants of upper Permian flora occur in addition to fauna. The cement in the sediments of

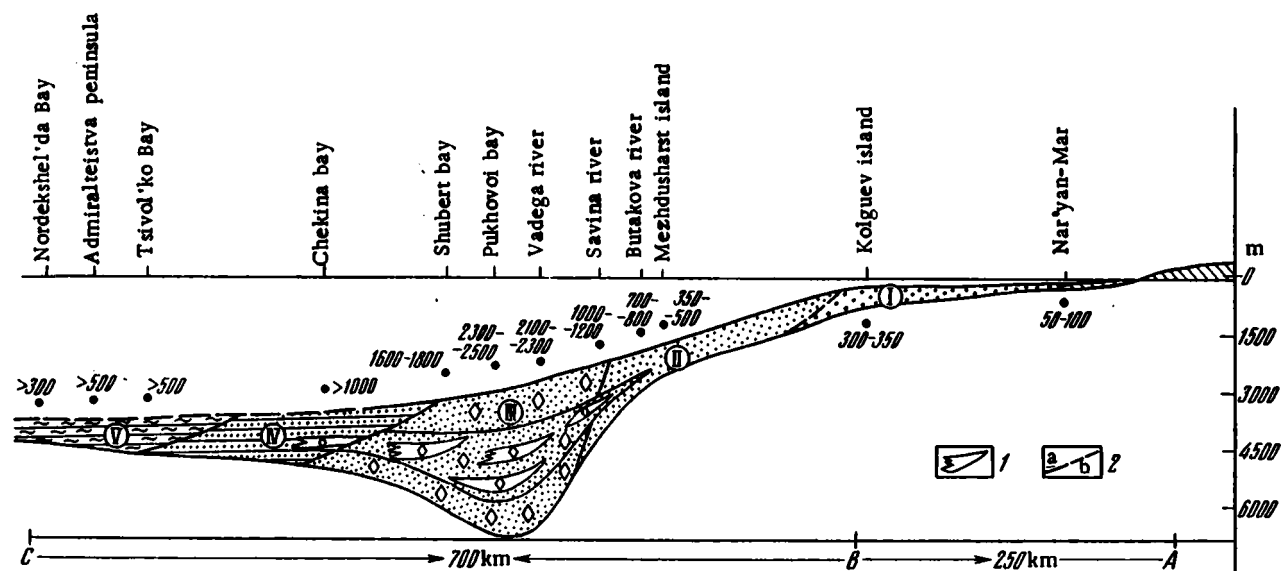


Fig. 2. Facies profile of upper Permian deposits along a line from the town of Nar'yan-Mar-Vaigach island--Novaya Zemlya: 1) olistostromes; 2) boundaries of facies zones [a) established, b) proposed]. Remaining symbols are as in Fig. 1.

the zone is generally clay, with no carbonate admixture. At the same time, sandstone olistoliths have carbonate-clay cement. In a series of cases, 5-8 centimeter crusts in which the carbonate has leached out are formed on their surfaces. In fragments of coarse shells brachiopods are often observed amid dissolution, and they suggest melting sugar lumps. Fine shells of brachiopods are sometimes almost completely dissolved, and only impressions and cores are seen in the rock. At the same time, in other olistostromal packets, fine brachiopod shells are preserved, and in the subsequent zone (the fourth zone) locations of Carboniferous foraminifera are known. The causes of selective carbonate solution are not completely clear. The authors propose that it is connected with the position of the basin floor close to the carbonate compensation level. The maximal thickness of sediments and the massive sedimentation of material from the sludge flows creeping on a slope makes it possible to consider the third zone as the foot of the slope. In formational relation the zone corresponds to wildflysch widely developed in a series of geosynclines.

The fourth zone extends to the north at 110-130 km from Krestovaya inlet on the west and Neznaemyi bay on the east. In this zone occur reduction in sediment thickness, disappearance of olistostromes, and the appearance of rhythmically structured packets with predominance of sand turbidites characterized by graded bedding; their quantity increases from south to north. The rhythmically constructed packets have thickness from a few tens of meters to 120 m and are composed of a series of rhythms (from 1 to 27 per packet). The thickness of individual rhythms varies from 1.5 to 7 m, most often 2-4 m. Complete rhythms have the following characteristics: 1) the sandstones are massive, fine grained, sometimes with graded bedding, 0.2-0.3 m thick; 2) the sandstones or siltstones are indistinctly interlayered or lenslike to wavy-layered, 0.2-0.5 m thick; 3) the argillites are indistinctly interlayered, often with textures of flow and sediment turbidation, 0.2-0.3 m thick.

The lines dividing the rhythms are generally wavy due to erosion and the uneven intrusion of sandstones into underlying argillites. Coarser grained material (to gravel size) is concentrated in pocketlike depressions, with multiple fragments of shells and sometimes foraminifera of Carboniferous age. The "a" and "e" intervals of the turbidite model are generally preserved in abbreviated rhythms, and the intermediate intervals are poorly expressed. Small boulders seldom occur in the scarce interlayers of olistostromes, and in general the fragments do not exceed gravel and sand sizes.

The entire zone on the whole represents the proximal facies zones of sand turbidites with their characteristic signs: cyclical structure, erosion and filling structures, and often expressed graded bedding.

The fifth zone lies to the north of the preceding. It is traced over 130 km from Og bay on the east to Nordenshel'd bay on the west. The section which corresponds to the Belshkinsk suite of the sequence here has a thickness of 400-500 m. The deposits are represented by distal turbidite facies and they are divided into three roughly even parts, with often completely arbitrary boundaries. The lower sequence represents alternation of homogeneous massive argillites and clay turbidites. The middle is distinguished from the lower by the presence of sparse interlayers of polymict silt-sandstones from a few to 80 cm thick. The upper sequence, built up at the base by clay turbidites, contains from 10-20% interlayers of polymict fine grained sandstones and silty-sandstones.

Most typical distal rhythms are represented by immature turbidites with poorly developed Bouma cycles, composed from two or three intervals (from the bottom upwards): 1) argillites of silty or silty-pelitic with lenslike to wavy or intersecting layering, 0.01-0.3 m thick; 2) argillites with vortical texture 0.05-0.4 m thick (often absent); 3) black massive argillites, 0.03-1.5 m thick.

On the whole, the fifth zone is characterized by the greatest reduction of sediment thickness, a sharp decrease in the role of sand material, the predominance of pelitic sediments, the clear rhythmicity of sequences, the absence of creep textures and olistoliths, and well sorted rocks. These signs indicate sedimentation of terrigenous material from suspension abyssal plain conditions, with sharp weakening in the energy of the turbiditic flow (the environment of a "fading" flow).

This is the northernmost zone, the last exposed on Novaya Zemlya.

We may draw the following conclusions.

Facies analysis of the upper Permian, Ufimian deposits of Novaya Zemlya and the northern part of the Timano-Pechorsk region make it possible to distinguish five facies zones in the

marine deposits developed here. The first of these, the southern, characterizes shelf deposits, the second, slope deposits, the third, the slope base, and the last two, deposits of the floor of the Permian geosynclinal basin.

In Permian deposits of Novaya Zemlya A. P. Lisitsyn [1] clearly noted a zone of avalanche sedimentation at the slope base of the continental slope on recent material; namely within its limits is a localized primary mass of terrigenous material which was brought from the slope edge by sludge flows. The sediment accumulation rate at the slope base of the Permian continental slope reached 2-2.5 km/million years. In formational relations the deposits developed here may be compared with the wildflysch widely distributed in geosynclines. Numerous olistoliths of more ancient rocks are transported by sludge flows on the continental slope downwards over many tens of kilometers, and it is therefore impossible to treat their location as proximal to a rocky shore.

In recent years a wider distribution of opinions has been found on whether geosynclinal flysch is analogous to oceanic turbidites. The production of this formation by the intensive input of terrigenous material into the basin occurs over a distance no less than 100 km from the base of the continental slope, beyond the zone of wildflysch accumulation. Indications occurring in the literature on the formation of flysch in narrow downwarps ("geosynclinal compression") of the sediment accumulation basin in a period of its transformation in a fold zone.

The question of the depth of the Permian new-land basin is most complicated. Since the rapid, in a geological sense instantaneous, (no more than 1 million years in time) accumulation of 2500 m of sediments did not lead to shallowing of the basin and a marked change of the facies environment, it would be possible to propose that the basin depth substantially exceeded 3000 m. However, it is also possible to explain this by the compensated downwarping of the basin floor under the heavy accumulation of sediments (Fig. 2).

A more reliable result is obtained by analysis of the dynamics of sediment accumulation. The amplitude of displacement of sludge flows reaches no less than 200 km. Since they did not simply creep and hence erode lithified Paleozoic rocks, entrapping olistoliths, the angle of the slope inclination could not be less than 1°. On the basis of this, the minimal basin depth is determined to be 3.5 km (probably somewhat greater).

The rocks of the second zone, which are correlated to continental slope deposits, still have an admixture of carbonate in the sandstone cements in the central part. In the north, bordering the slope base, carbonate is absent from the cement, while distinctly expressed signs of leaching of carbonate are observed in the third zone.

This situation, in opinion of the authors, may indicate the position of the basin floor close to the carbonate compensation level.

LITERATURE CITED

1. A. P. Lisitsyn, "Avalanche sedimentation," in: *Avalanche Sedimentation in the Ocean* [in Russian], Rostov Univ., Rostov-on-Don (1982), pp. 3-58.
2. F. I. Entsova, M. V. Konovalova, R. P. Slivkova, and V. D. Tel'nova, "New data on the stratigraphy and oil and gas potential of northern regions of the Timano-Pechorsk provinces," in: *Geology and Oil and Gas Potential of the North-Eastern European Part of the USSR* [in Russian], No. II, Nauka, Syktyvkar (1972), pp. 145-158.
3. F. I. Entsova, V. D. Tel'nova, S. G. Grinchenko, et al., "Permian deposits of Kolguev island," *Sov. Geol.*, No. 8, 70-76 (1981).
4. *Basic Features of the Stratigraphy of the Permian System of the USSR* [in Russian], Nedra, Leningrad (1984).
5. *Permian Deposits of Novaya Zemlya* [in Russian], Nauka, Leningrad (1981).
6. L. G. Povysheva, "Results of mineralogical analysis of the heavy fraction of terrigenous rocks from Yuzhnaya island, Novaya Zemlya," in: *Geology of Yuzhnaya island, Novaya Zemlya* [in Russian], PGO "Sevmorgeologiya," Leningrad (1982), pp. 58-67.
7. L. G. Povysheva and V. I. Ustritskii, "Creep structures in Permian deposits of Yuzhnaya island of Novaya Zemlya," in: *Upper Paleozoic and Mesozoic Islands and Coasts of the Arctic Sea of the USSR* [in Russian], NIIGA, Leningrad (1979), pp. 27-33.
8. L. G. Povysheva and V. I. Ustritskii, "The composition of the heavy fraction of terrigenous sedimentary rocks of the Permian from the northern European part of the USSR, and its value for paleogeography," in: *Upper Paleozoic and Mesozoic Islands and Coasts of the Arctic Sea of the USSR* [in Russian], NIIGA, Leningrad (1979), pp. 10-26.

9. N. N. Sobolev, V. I. Ustritskii, and G. E. Chernyak, "The structure of the Paleozoic passive continental margin on Novaya Zemlya," in: The Geological Structure of the Barents-Karsk shelf [in Russian], PGO "Sevmorgeologiya," Leningrad (1985), pp. 34-43.
10. V. I. Ustritskii, "On the correlation of the Urals, Pai-Khoi, Novaya Zemlya, and Taimyr," Geotektonika, No. 1, 51-61 (1985).

EARLY PRECAMBRIAN METASEDIMENTARY ROCKS IN RELATIVE COMPARISON WITH RECENT CONTINENTAL MARGIN DEPOSITS

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Analysis of early Precambrian sedimentary deposits was conducted. On the basis of a complex of lithological, paleogeographical, and paleotectonic indications we distinguished among three groups of formations formed in various geologic environments: on continents, in marginal basins, and in oceans.

Opinions existing earlier on the practical unrecognizability or the extreme fragmentation and nonuniqueness of indicators on the environment of Precambrian sediment accumulation has gradually given way to the general recognition of the fundamental possibility of uncovering the history of Precambrian sedimentogenesis [1, 5, 8, 10, 11, 15-17, 19]. At the present time, reconstructions of environments of rock and ore formations during early stages of the Earth's development, first attempted by V. E. Logan and P. A. Puzyrevskii, later by A. A. Inostrantsev and I. I. Sederholm, and in our time in the articles of Kh. Vyayuryunen, P. Eskola, and L. Ya. Kharitonov, and many other later investigators, has obtained wide development and become the general methods of work in areas of Precambrian development, in fact in all of the countries of the world [16, 19].

Geochemists [2, 14], tectonicists [1, 3, 13, 21], general geologists [10, 15, 25], and paleoceanologists [9, 12, 24], conduct arguments on the existence of a continent-ocean system and consequently, continental and oceanic sediment accumulation environments, beginning with the Archean. However, groups of scientists doubting or even actively denying the existence of early Precambrian oceans are numerous [20]. In both cases sedimentary deposits properly are either analyzed only from the most general positions, or they generally drop out of consideration. Meanwhile, "it is first of all necessary to demonstrate the existence of ancient oceans by means of searching for ancient abyssal-pelagic oceanic deposits and analysis of their spatial interrelations with shallower water marine facies, that is, by searches for the analogs of contemporary oceanic facies" [20, p. 4].

The achievements in the study of the geology of oceans and seas [4, 6, 7, 18, 22, 23] indicates the extremely variable composition and the variety of lithogenetic types of deposits which are characteristic of pelagic parts of the ocean, its islands, and continental margins. Features such as the wide development of zones of terrigenous clastic and volcanoclastic deposits on the shelf limits and in the oceanic abyssal zones, the combination of structural-textural indications, and the type of stratification which indicates their sedimentation under conditions of periodically active autokinetic flows (mass flows) all present special interest. The close association of such deposits with finely-elutriated, biogenic-chemogenic, truly deep water, oceanic deposits (so called red clays), and the sharp subordination of the latter's value in the structure of the sedimentary cover of contemporary oceans is extremely significant. Although the main genetic point of this fact remains not yet completely clear, it is evident that previous representations of terrigenous deposits as typomorphic formations of continents requires review, and in significant refinement. It is also clear that in a relative comparison plan, rock associations are somewhat more informative than taking deposit types individually, while in connection with this, associations of terrigenous detrital deposits as the sediments that are the most "conservative and independent" of evolution [22] have the primary value.

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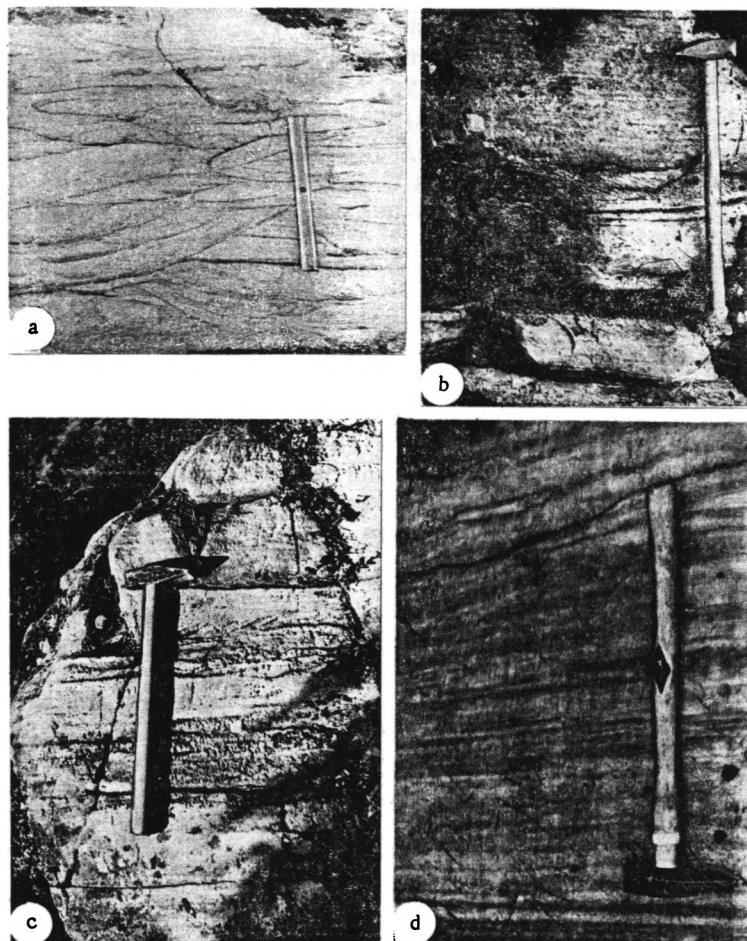


Fig. 1. Type textures of metasedimentary continental deposits of early Precambrian age. Yatulii, lower Proterozoic. Eastern part of the Baltic shield: a) medium grained quartzite-sandstones, well sorted, with cross beds accentuated by martite; b) the same, with horizontal layering, with interlayers of siliceous, coarse-grained, quartzitic metapsammites; c) quartzite-sandstones of coarse-grain size, poorly sorted, carbonate, with unidirectional cross-beds alternating with massive and horizontally layered medium and fine-grained sericitic quartzite-sandstones; d) quartzites of mixed fine and medium grain sizes, horizontally layered with ripple marks.

TYPES OF EARLY PRECAMBRIAN DEPOSIT ASSOCIATIONS

All of the various authentic sedimentary deposits from the early Precambrian may be reduced into three metasedimentary rock associations that are essentially distinct in their formation conditions.

In the first group are associations of terrigenous and chemogenic-biogenic deposits, whose genetic signs (compositions, structure, texture, body geometry, contacts, morphogenetic characteristics of accessories, geochemical parameters, surrounding formation) and the results of paleogeographic reconstructions make it possible to unambiguously define the conditions of their formation as typical of continental segments of earth's crust (Fig. 1). Typomorphic representations of this type of associations are the Yatuliisk deposits of Central Karelia, terrigenous rocks of the Rand and Terkva basins in Africa, quartzite-conglomeratic sequences of the Blind River on the Canadian shield, and copper-bearing deposits of Udokan in Siberia [10, 11, 15].

Among deposits in the first group of associations are distinguished eluvial, deluvial-creep, flow, river-mouth, coastal, overdrying waters, basins with active near-bottom wave action, and basins in which wave action does not reach the floor. As a rule they are all weakly

dislocated, metamorphosed no higher than the biotite isograd of the greenschist facies, and they contain essentially every combination of their initial genetic characteristics [1, 2, 8, 10, 11, 15-17].

According to the results of paleogeographic and paleotectonic constructions, deposits of the first group are separated into continental, transition (coastal-marine), and marine associations. They generally alternate conformably with one another in the section and are substituted over area, thereby reflecting lateral inhomogeneity and the interchange through time of sediment accumulation environments. In complete sections it is possible to trace a discontinuous succession of interchange through time of continental deposits followed by marine deposits followed again by continental, that is, complete transgressive-regressive cycles of development of sedimentation basins. The purposefully directed study of such successions and the tracing of their compositional elements over area [10, 11, 15] establish the discontinuous lateral interchange of deposits from continental to marine, that is, the environments of the above water part of continental dry land interchange in time with the environments of the underwater continental margins. From this it follows that the mechanism of transgression and regression operated in Precambrian time, possibly analogous to that which later was provided by interaction of continents and oceans.

The metasediments of the second and third groups of lithogenetic associations of early Precambrian rocks serve as potential material demonstrations of the existence of environments comparable to the environments of continental margins and oceans.

The second group of early Precambrian age unites associations of metaterrigenous deposits (metapelites, metasilts, metapsammites, partially metapsephites) with the characteristic graded bedding and rhythmicity of the turbidite type (Fig. 2). By a combination of typomorphic signs, the majority of which well are preserved right up to palinogenesis [5, 10, 15, 19], they correspond to deposits generally united by the general term turbidite. The Svecofennian of the Baltic shield are the type representations of such deposits [10]. Three closely connected types of turbidite metasediments are distinguished, corresponding to fluxoturbidites, turbidites, and contourites [22, 23].

Fluxoturbidites are represented by rhythmically alternating metasilts, metapsammites, and metapsephites in proportions varying from essentially metapelite-metapsammite composition to the complete disappearance of metasilty-pelitic and/or metapsammite deposits from the section. The other characteristics of the rhythms are also extremely varied: the structure, contacts, thickness, composition, and structure and texture of deposits.

The graded type of rhythms occur more often (the size of the detrital fraction in the rhythms decreases upwards), but there are also often cases of rhythmicity of inverted-graded structure (the size of the detrital fragments increases upwards). The contacts are straight and sharp, seldom gradual. The thickness of the elemental rhythms varies within the limits of tens of centimeters to a few meters, and they are grouped in rhythms of coarser sequences, reaching tens and hundreds of meters.

Two types of fluxoturbidites are distinguished by their material composition: 1) built by the products of the solution of granitoids and metamorphites (that is, rock associations of the continental type of the Earth's crust); 2) built by fragments of sedimentary and volcanogenic rocks of basic and more seldom ultrabasic composition, which are more characteristic of island arc systems and the floor of contemporary oceans. By intensive metamorphism the first are transformed into conglomerate-containing mica-feldspar gneisses, and the second are transformed into amphibole-biotite gneisses and schists or various "leptinoids" with interlayers of laminated conglomerates.

Conglomerates containing the lower members of the rhythms (seldom the concluding members), are distinctive in the weak unloading of fragments (pudding parts), and the displacement of fractions by various degrees of reworking and size. Generally the arrangement of boulders and pebbles indicates their transport in the suspended state and the settling into the sediments from suspension. The initial structure of the metapsammites (the middle member of the rhythms) and metapelites (the upper member of rhythms), with few exceptions, is completely transformed by metamorphism; their texture is practically not varied.

The texture of the fluxoturbidites is massive and indistinctly layered with gradual transitions between the layers. The layering becomes more distinct and thin towards the top of the rhythms, in proportion to the decrease of granularity; crossbedded layering of the flow type are sometimes noted in the lower part of the metapsammite layers, and graded bedding

is noted in the upper part and in the metapelites. Fine layers of metasilicate and metacarbonate-silicate (millimeters, seldom centimeters), and sometimes highly ferrous sediments are occasionally noted on the rhythm boundaries.

Turbidites are distinguished from fluxoturbidites by the absence of metapelite, the significantly greater role of metasilstones, the smaller thickness of the rhythms (tens of centimeters), the generally better sediment sorting, and the predominance of finely graded bedding in the parts of the elemental rhythms. Two and three member, and seldom four member rhythms, are usual. More complete rhythms, in practice completely fulfilling the ideal model of A. H. Bouma [22], are also distinguished in individual cases. The rhythms begin with metapsammites and metasilstones with crossbedded or massive bedding, above graded bedding. In the middle part they are built up by metasilstones, finely alternating with metapsammites, and they conclude with metasilstones and metapelites with graded or finely horizontal texture. Interlayers of inverted graded structure are sometimes observed in the upper rhythms: "flame" type textures, neptunian dikes and intrusive dikes, and underwater layer creep textures occur.

Contourites combine rhythms of well sorted finely graded-bedding metasilstones and metapelites, sometimes with the admixture of finegrained psammites. The sequence of layers reaches from millimeters to 10 cm. The distinctive features of contourites are, in addition, sharp lower and upper layer boundaries and the absence of traces of erosional cuttings.

Fluxoturbidites, turbidites, and contourites are developed both together, in the form of combined parts of single rhythms, and in the form of continuous lateral facies arrays, where they are connected with one another by gradual vertical and horizontal intertransitions. With the predominance of one or another variety of rhythms independent lithogenetic associations are isolated: fluxoturbidite, turbidite, and contourite. Alternating with one another, they cause rhythmicity of lower orders, up to megarhythms. Three basic types of vertical and horizontal successions are distinguished: 1) from fluxoturbidites or turbidites to contourites; 2) from fluxoturbidites or turbidites through contourites again to fluxoturbidites (turbidites); 3) from contourites and/or turbidites to fluxoturbidites and subsequently again to turbidites and contourites. The first and second type of successions most often characterize the beginning of megacycles; intrinsic to them are primarily rhythms formed by the redeposited products of erosion of continental rock types (granitoids, gneisses, crystalline schists, quartz), and the interchange in time of volcanogenic rocks of basic or basic-intermediate composition. The third type of succession is correlated to the middle of transgressive-regressive megacycles. They are distinguished by volcanoclastic or mixed composition of detrital fractions of metasediments and associations from extrusive rocks of mid-acid and acid composition downwards and basic-ultrabasic upwards.

In agreement with experimental data and the results of study of recent sediments from seas and oceans [6, 7, 18, 21, 22], turbidite sediment accumulation signifies the activity of a specific type of sludgy flows (pastelike, granular, suspended), which are known to function [22, 23] mainly in canyons of the continental slope, at the foot of the continental slope, and in abyssal and bathyal troughs. Fluxoturbidites signify an initial immature stage of the development of such flows, and turbidites and contourites signify the stage of their maturing and dying out. Their complete array displays the directed decrease of the hydrodynamic flow power over time in proportion to the remoteness from its place of origin to the place or time of its dying out. In the most general and schematicized form, such direction corresponds to the lateral succession of marginal-continental deposits with deposits of the continental margins and abyssal troughs of oceans. In connection with this rather general association of interlayers of carbonaceous-siliceous and carbonate-siliceous metamorphosed rocks, lithologically comparable to oceanic plain deposits, with contourites for early Precambrian deposits is extremely significant and indicative. They compose the characteristic feature of third group of early Precambrian metasedimentary rocks.

The third group of metamorphosed sedimentary deposits of early Precambrian age unites rocks whose depositional environments are least clear. These are primarily various slates and fine-grained quartzites, arising as a result of recrystallization by metamorphism or carbonate-mud, silicic, and clay deposits, sometimes enriched by carbon, sulfur, and iron, as well as vanadium, nickel, cobalt, and a series of other metals. The main features of such deposits are submicroscopic horizontal layering, indicating an extremely passive hydrodynamic sedimentation regime, their association with metatuffogenic deposits and lavas of basic-ultrabasic composition, and their correlation with temporal intervals of maximum development of

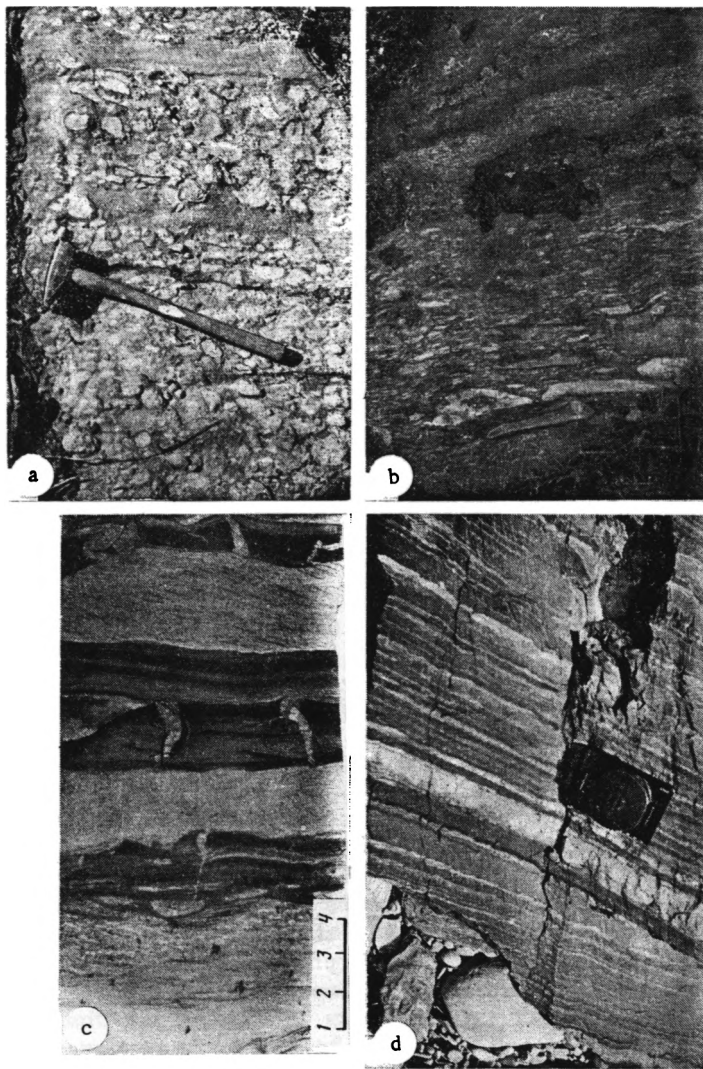


Fig. 2. Type textures of turbidite deposits of the early Precambrian. Svecofennian, lower Proterozoic, from the eastern part of the Baltic shield: a) medium and coarse pebbly conglomerates, rhythmically alternating with metagreywacke from the lower part of the fluxoturbidite microrhythm; b) the tye structure of the fluxoturbidite microrhythm: conglomerates, transforming above into graded bedded greywacke; c) turbidites, represented by alternating layers of massive cross-bedded psammites, replaced upwards by graded bedded shales on silty-pelites; d) shales with the finely rhythmic textures of contourites.

transgression. They form the comparatively well traced so-called black shale levels of the type Yalonovarsk ore bearing horizon from the upper Archean and the Zaonezhsk horizon from the lower Proterozoic of Karelia.

There exists similarity in the regularities of the stratigraphic correlation of such levels [15] with regularities in the appearance of the Cretaceous global "thalassogenic" levels of black shales, which distinguish stages of "global oceanic events in the development of a reducing environment" and the maximum opening of oceans. P. P. Timofeev and L. I. Bogolyubovii [20] showed that black shales formed in both relatively shallow water and in deep water conditions.

In connection with this, the space-time associations of the considered early Precambrian rocks with volcanogenic formations of the tholeiite series and turbidite deposits have a more defined value [5, 15] in the absence of reliable signs of their direct connection with continental facies and the facies of coastal shallow water [10].

RELATIVE-COMPARATIVE ESTIMATE OF ENVIRONMENTS OF EARLY PRECAMBRIAN SEDIMENTATION

It is evident that the three principally distinguished groups of metasedimentary deposits of early Precambrian age correspond to three sharply distinguished environments of sediment accumulation.

The combination of lithologic-facies indicators of rocks assigned to the first lithogenic group of deposits is so informative that their continental occurrence is recognized by all investigators. Consequently, the existence of early Precambrian continents is also recognized. Signs of similar formations are already noted in the early Archean (from 3500-3000 million years ago), but they obtained rather wide development only in the early Proterozoic, mainly beginning from 2800-2600 million years ago [1, 5, 8, 10-12, 14, 15].

Continental deposits characterize structures of isometric form, and are distinguishing by simple, comparatively mild sloping folding, low degrees of metamorphism (greenschist facies), the absence or sharply limited manifestation of granitoid magmatism, lateral variation in the facies composition of rocks, and by thicknesses within the limits of hundreds, seldom thousands, of meters.

The interpretation of the accumulation environments of the second (turbidite) and third (thalassogenic) groups of early Precambrian deposits is incomparably less defined. Many investigators consider them as typical shallow water sediments, and such an interpretation for the Precambrian is apparently considered most valid. The conglomerates, breccias, sandstones, crossbeds, erosional layer contacts, the many angles of rock cracking due to diagenesis which have been erroneously assumed to be drying fractures, and the similarity of ripple marks are all assumed to be absolute indicators of shallow water. However, as has become well known in recent time, all of these signs are also distinctive in rocks of the oceanic sedimentary cover. While turbidite deposits are concentrated in underwater canyons, mainly at the continental slope-foot, they are also widely developed in abyssal troughs, that is, in clearly deep water parts of oceans, at great distances from regions of contemporary continental sediment accumulation. In light of this it is extremely significant that the Precambrian turbidite deposits are found in normal stratigraphic interrelations with metasediments which are lithologically similar to deepwater deposits, and with volcanic rocks of the tholeiite series, while their contacts with unconditionally continental deposits most often have a clear tectonic origin. The turbidite deposits are, as a rule, deeply metamorphosed, crumpled into isoclinal folds, often granitized, while the deposits of proposed thalassogenic origin are deformed and on the whole they are clearly metamorphosed less intensely.

Thus, the objective state of factual material on the lithology of the early Precambrian is such that among sedimentary rocks peculiar to it, it is entirely legitimate to consider possible analogs to deposits of the contemporary structure of continental margins and oceans. Turbidite clastites are related to the former, while siliceous, carbonaceous, and other slates which distinguish the epochs of greatest early Precambrian transgressions are related to the latter. Both occur, beginning with the Archean, while relative to them the importance diminishes with time among lasting sedimentary deposits. Characteristics include a linear component to their structure, the correlation of such structures to belts along megablock boundaries, their complexly folded scaly-fault structure, the clear remnant-erosional nature, the overall insignificant thickness of individual metasediment interlayers (tens, seldom a few hundreds of meters of thickness for thalassogenic deposits, and hundreds, seldom thousands of meters of thickness for turbidite deposits) for the sharp predominance over the sediments of metavolcanics that are petrochemically similar to oceanic and island arc types.

From all of this it follows that in relative plan among early Precambrian deposits of the contemporary continents and the tectonic structures composing them, formations are established that are similar to both continental and marginal-continental, and to oceanic types. They are closely interconnected between themselves, often alternating and replacing one another laterally [10]. Such correlation introduces a series of questions, the answer to which has, possibly, an underlying value for understanding the history of the development of lithosphere.

Another mainpoint here involves the explanation of whether the resemblance of variously aged lithological (petrological) rock associations (structural-material units [1]) indicates the uniformity of their formational environments. Such characteristics have a defining value in this plan and they are caused by the irreversibility of the Earth's development as a regularly evolving cosmic body.

One of the most obvious features of Precambrian sediment accumulation is the absence of subaerial vegetation, and consequently the barren subaerial landscape. The consequence of this must have been the more active influence of the transporting role of pastelike, granular, turbidite (suspended) flows and the wind than in the Phanerozoic, and it means a more significant value for the terrigenous deposits of closed water basins of the early Precambrian in comparison with their Phanerozoic analogs. It is understood, that as a result of this, similar landscape environments of early Precambrian and Phanerozoic time could be distinguished from one another by the typomorphism of rock associations, their thicknesses, geochemical parameters (for example, potassium behavior), etc. All of these, however, depend on many other parameters of exogenesis. In particular, their connection with the relief of the dry land the floor of the water basins is evident. It is customary [3, 8, 14, 15, 25] to consider this relief to have been distinguished by a smaller separation. If this was actually so, then a lesser separation of relief should have assisted in reduction in the activity of the agents of detrital material transport, and consequently, some leveling of features caused by the absence of vegetation on the continents.

It is an established fact that there is an increase (in proportion to deepening in the geologic history) in the value in the composition of regions of erosion of crystalline rock, particularly of metamorphites and formations of the mafic series [8, 10, 12, 14, 15, 19, 24]. A significant decrease is noted in the thickness and maturity of remnant products (eluvia) of the early Precambrian weathering crust [10, 11, 19], but whether this indicates less intense disintegration of rocks of subaerial regions and the particular weathering conditions, or that this is a consequence of a decrease of the degree of preservation of alluvial formations in the depths of geologic history remains unclear. Estimates of the effects of life systems on Precambrian sedimentation are also ambiguous. It is certain that such systems existed and could have had a defining value both on the stage of disintegration of rocks from the supply regions, and for sediment accumulation in closed water basins [17].

The concept of moderate separation of early Precambrian dry land is generally linked with opinions on the decreased thickness of the Earth's crust at this time, on the high endogenic transmission of the early Precambrian lithosphere, the more active influences of endogenic gases and hydrotherms on sediment accumulation than in the Phanerozoic, and on the specific geochemical regime of the early Precambrian sedimentogenesis [8, 10, 11, 12, 14, 19]. It is evident that all of these features exerted more or less significant influences on the typomorphic rocks of the sediment accumulation environments, and that consequently, identical or nearly identical landscape environments of the post Precambrian and Precambrian could be distinguished by one or another parameter of the rocks recording these environments, while an identical combination of individual parameters could arise under more or less distinct natural conditions. From this follows the necessity of maximally complete consideration, and the comparison of all possible sedimentary rock characteristics in their associative connections and the space-time conformities of parameter variations of these connections. Therefore, for genetic judgment it is important to study sedimentary deposits not in isolation, but together with the magmatogenic formations accompanying them, with consideration of the features of structural deformations and paleotectonic characteristics, metamorphic conformities, and metasomatism. The results of such investigations correspond to the concept of an early Precambrian origin of continents and oceans and their interactions, starting at least at a limit of 3800-3500 million years, as Ch. B. Borukaev, L. I. Salop, and other investigators reasoned. Taking such an interpretation of the sedimentary deposits of the early Precambrian and with its aid tracing the succession of changes in time and space of corresponding groups of sedimentary rocks, and consequently, of their formational environments as well, it is necessary to note the interchange of diverse types of sediment accumulation environments both in area and in time. Two complete space-time series are noted at the contemporary level of knowledge on the early Precambrian, each of which begins and concludes with continental or marginal-continental groups of sediments, while the middle part contains rocks comparable with oceanic deposits: lower Proterozoic (Karel'sk, Afebiisk, and age analogs). Consequently, it is necessary to assume that in the early Precambrian, after the formation of the first continents, and the Earth's crust within the limits of the contemporary continents, complete cycles of transformation from the continental to the oceanic and back to the continental state occurred at least twice prior to achieving the final continental state in the late Proterozoic. It is still scarcely possible to recognize such an assumption as sufficiently justified, and consequently, it is conditional until the typization of early Precambrian rocks on basis of their

resemblance to deposits of contemporary environments of sediment accumulation. Nonetheless, such analysis of Precambrian formations is fruitful and for the present unique, by means of the objective interpretation of features of early Precambrian sediment accumulation.

On the basis of the above, it is possible to draw the following conclusions.

A group of rocks formed on the continents is established among early Precambrian meta-sedimentary deposits, and less uniquely, formations which correspond to the complex of indicators of marginal-continental deposits and deposits of recent oceans. Taking into consideration the specifics of Precambrian sediment accumulation, it is possible to suppose that such similarity has only a comparative value at the present time, and is indicative of the similarity but not the identity of environments of marginal-continental and oceanic types in the early Precambrian and Phanerozoic.

The typing of metasedimentary rocks on the comparative basis of the entire available complex of lithological, paleogeographical, and paleotectonic signs is the most fruitful and single sufficiently valid method for the study of features of early Precambrian sediment accumulation, and consequently, also the uncovering of the history of the origin and evolution of the global ocean and continents. The selective comparison of individual factors, types of rocks, and the characteristics of individual rock associations may lead to fundamental errors.

LITERATURE CITED

1. Ch. B. Borukaev, The Structure of the Precambrian and Plate Tectonics [in Russian], Nauka, Novosibirsk (1985).
2. A. P. Vinogradov, Introduction to the Geochemistry of the Ocean [in Russian], Nauka, Moscow (1967).
3. R. G. Garetskii and A. L. Yanshin, "Deepwater sediments of fold regions," in: History of the Global Ocean [in Russian], Nauka, Moscow (1971), pp. 278-282.
4. The Geology of Continental Margins [Russian translation], Vol. I, Mir, Moscow (1978).
5. K. Condie, Archean Greenstone Belts [Russian translation], Mir, Moscow (1983).
6. A. P. Lisitsyn, Processes of Oceanic Sedimentation [in Russian], Nauka, Moscow (1978).
7. N. V. Logvinenko, Marine Geology [in Russian], Nedra, Leningrad (1980).
8. V. A. Melezhik and A. A. Predovskii, The Geochemistry of Early Proterozoic Lithogenesis [in Russian], Nauka, Leningrad (1982).
9. A. S. Monin and Yu. A. Shishkov, History of Climate [in Russian], Gidrometeoizdat, Leningrad (1979).
10. V. Z. Negrutsa, Early Proterozoic Stages in the Development of the Eastern Part of the Baltic Shield [in Russian], Nedra, Leningrad (1984).
11. T. F. Negrutsa, The Paleogeography and Lithogenesis of the Early Proterozoic in the Region of the Junction of Karelides and Belomorides [in Russian], Leningrad State Univ. (1979).
12. Paleooceanology, Colloquium. 03. Reports 27th IGC, 3, Nauka, Moscow (1984).
13. A. V. Peive, A. L. Yanshin, L. P. Zonenshain, et al., "Formation of the continental Earth's crust in Northern Eurasia (in connection with the construction of a new tectonic map)," Geotektonika, No. 5, 6-23 (1976).
14. A. B. Ronov, The Sedimentary Cover of the Earth (Quantitative Regularities of Structure, Composition, and Evolution) [in Russian], Nauka, Moscow (1980).
15. L. I. Salop, The Geological Development of the Earth in the Precambrian [in Russian], Nedra, Leningrad (1982).
16. A. V. Sidorenko and O. I. Luneva, Towards a Question on the Lithologic Study of Metamorphic Sequences [in Russian], Izd. Akad. Nauk SSSR, Moscow-Leningrad (1961).
17. A. V. Sidorenko, V. A. Tenyakov, S. A. Sidorenko, et al., The Precambrian and Problems in the Formation of the Earth's Crust [in Russian], Nauka, Moscow (1978).
18. N. B. Vassoevich, V. A. Librovich, and N. V. Logvinenko (eds), Handbook on Lithology [in Russian], Nedra, Moscow (1983).
19. Thesis Abstracts, V. II, S. 05.05, Nauka, Moscow (1984).
20. P. P. Timofeev, V. N. Kholodov, and I. V. Khvorova, "The evolution of sediment accumulation processes on continents and in oceans," Litol. Polezn. Iskop., No. 5, 3-23 (1983).
21. V. E. Khain, "Features of the tectonic development of the Earth's crust in the early Precambrian - factual and imaginary," in: Problems of Early Precambrian Geology [in Russian], Nauka, Leningrad (1977).
22. I. V. Khvorova, "Terrigenous detrital deposits of oceans and some seas," Litol. Polezn. Iskop., No. 4, 3-23 (1978).

23. I. V. Khvorova, Volcaniclastic accumulations in the sedimentary cover of the oceans," *Litol. Polezn. Iskop.*, No. 1, 3-25 (1980).
24. T. Shopf, *Paleoceanology* [Russian translation], Mir, Moscow (1982).
25. A. L. Yanshin, "Deepwater deposits of the geological past," in: *Problems of Recent Lithology and Sedimentary Mineral Resources* [in Russian], Nauka, Novosibirsk (1977), pp. 4-7.

PETROMAGNETIC ANALYSIS OF THE DEVONIAN ROCKS
FROM THE PRIPYAT DEPRESSION

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The lithologic-petromagnetic method includes kappametry of cores (lithologic magnetic investigations) and magnetic-fractional-mineralogic analysis (MFMA) [1]. Lithologic-magnetic studies are conducted for layer-by-layer field investigation of borehole sections for rapid characterization of the magnetic properties of rocks (susceptibility χ) in the section intervals represented by the drill core. The results of kappametry are presented as diagrams reflecting the different features of lithologic varieties according to the specifics and quantitative contents of magnetic materials of various classes (dia-, para-, antiferri-, or ferrimagnetic), their morphologies, paragenetic relationships, and alteration degrees. In the sedimentary bed the study distinguishes: layers and thin interlayers of volcanogenic rocks, ferruginous carbonates, and iron-containing silicate minerals (glauconite, chlorite, etc.). Diamagnetic interlayers and accumulations have zero susceptibility: these are "pure" varieties of calcite, anhydrite, gypsum, rock salt, coal, etc. Lithologic-magnetic analysis is a convenient method for dividing and correlating sections, especially if biostratigraphic studies and commercial geophysical exploration fail to provide unequivocal results.

Mineralogic-facies features of rocks of a composite lithologic habitus that cannot be revealed in microscopic investigations are registered by kappametric curves.

Petromagnetic analysis is a laboratory method used to investigate samples of all lithologic rock varieties selected according to core kappametric data. Petromagnetic analysis is based on dividing rock powders by magnetic separation. Provided an exact registration of separation currents, the fractions are characterized by a weight-percentage content and magnetic susceptibility. Petromagnetic analysis yields composite petromagnetic characteristics, denoted by four-character symbols. Figure 1 gives a generalized scheme of petromagnetic notation of magnetic mineralization of rocks. Rocks are divided into three groups: 1) predominantly paramagnetic; 2) weakly paramagnetic-diamagnetic; and 3) mainly ferrimagnetic [2].

Each group is defined by a set of four characters. Since the MFMA method is little known, we will describe the notations of the basic parameters and coefficients defining the elements of petromagnetic notation.

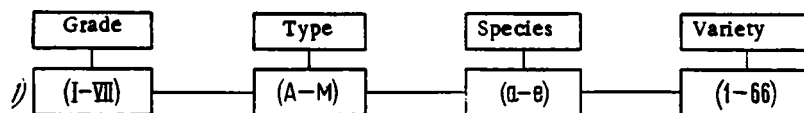
$\Pi_{M_{max}}$, $\Pi_{M_{pr}}$, and $\Phi_{M_{max}}$ are weight contents of magnetic fractions (as a percentage of the initial weighed amount); $\Pi_{M_{max}}$ and $\Pi_{M_{pr}}$, highest and intermediate magnetic fractions in paramagnetic separation mode (0.25-1.6 A); $\Pi_{M_{max}}$, magnetic fraction that represents the bulk of the rock; $\Pi_{M_{pr}}$, largest of the insignificant magnetic fractions of rocks, most of which remain in the nonmagnetic fraction; and $\Phi_{M_{max}}$, maximum magnetic fraction in the ferrimagnetic separation mode (0.0-0.2 A). $C_{M_{0.2}}$ is the weight content of the fraction isolated in the ferrimagnetic separation interval (0.0-0.2 A). For weakly magnetic rocks $C_{M_{0.2}} = \Phi_M$; for strongly magnetic rocks the parameter $C_{M_{0.2}}$ is the sum $\Phi_{M_{0.01}} + \Phi_{M_{0.025}} + \dots + \Phi_{M_{0.2}}$.

The grades are determined by the following values of the parameter $C_{M_{0.2}}$:

Grades	I	II	III	IV	V	VI	VII	VIII
$C_{M_{0.2}}$	0.01	0.00— 0.09	0.1—0.99	1.0—4.99	5.0— 14.99	15.00— 29.99	30.00— 50.00	>50.0

$I_{\Pi_{M_{max}}}$, $I_{\Pi_{M_{pr}}}$, and $I_{\Phi_{M_{max}}}$ are current intensity (amperes) at which the characteristic magnetic fraction is isolated in the specimen; Π_H is the weight content of the nonmagnetic fraction isolated at the maximum separation current (1.6 Å). E , E_ϕ , and E_H are coefficients expressing the ratio of the measured quantities $\chi_{\Pi_{max}}$, $\chi_{\Pi_{max}}$ and Π_H to χ_{Π_1} , $\chi_{\Pi_{0.2}}$, and $\chi_{\Pi_{1.6}}$; A is com-

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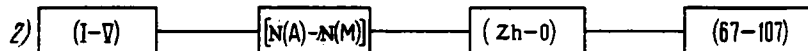


(I-VII) determined by the parameters $C_{M_{0.2}}$ with values $<0.01-50\%$

(A-M) determined by values of the parameter $I_{\Pi M_{max}}$ in the range $0.25-1.6, A$

(a-e) determined by values of the coefficient $E_i = \frac{X_{\Pi M_{max}}}{X_{\Pi i}}$ in the range $<55-500\%$

(1-66) determined by values of three parameters: $I_c, \Pi_{M_{max}}, \Pi_H$

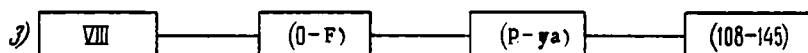


(I-V) determined by values of the parameter $C_{M_{0.2}}$ in the range $<0.01-14.99, \%$

[N(A)-N(M)] determined by values of the parameter $I_{\Pi M_{np}}$ in the range $0.25-1.6, A$

(zh-o) determined by values of the coefficient $E_H = \frac{X_{\Pi H}}{X_{\Pi 1.6}}$ in the range $<40-500, \%$

(67-107) determined by values of three parameters: $I_c, \Pi_{M_{np}}, \Pi_H$



VII determined by values of the $C_{M_{0.2}}$ in the range $>50, \%$

(o-f) determined by values of the parameter $I_{\Phi M_{max}}$ in the range $0.005-0.2, A$

(p-ya) determined by values of the coefficient $E_{\Phi} = \frac{X_{\Phi M_{max}}}{X_{\Phi 0.2}}$ in the range $<100-8000, \%$

(108-145) determined by the values of three parameters: $I_c, \Phi M_{max}, \Pi_H$

Fig. 1. Petro-magnetic notation of magnetic mineralization.

puted from experimental data; E and E_H can be less than or more than 100%; they define, respectively, the levels of paramagnetization or latent ferrimagnetization; E_{Φ} is always greater than 100% and determines the level of overt ferrimagnetization; and I_{ts} is the range of separation current modes (amperes) within which magnetic fractions (ΠM or ΦM) greater than 1% are identified.

The main term of the four-character notation is the type of magnetic mineralization. It estimates for genetically different rock varieties their magnetic state: antiferriparamagnetic (type A), paramagnetic (types B-M), weakly paramagnetic-diamagnetic (types N(A)-N(M)-N), and predominantly ferrimagnetic (types O-F).

The remaining three symbols specify additional characteristics: the grade indicates the degree of overt manifestation of ferritic mineralization; the species characterizes the covert manifestations of ferrimagnetic mineralization (species d, e, n, and o), the specific signs of superparamagnetic mineralization (a), and the degree of rock paramagnetization. Variety indicates the type of poly- or monomagnetization. In paramagnetic varieties, monomagnetization decreases in the direction 1 $\rightarrow$ 66 (because of strengthening of paramagnetic connections of weak paramagnetics with diamagnetics); in weakly paramagnetic-diamagnetic rocks, polymagnetization declines in the direction 67 $\rightarrow$ 107. The groundmass of rocks of species 107 usually consists of weak paramagnetics, v, which are to some degree associated with diamagnetics or with a mix of diamagnetics combined with a minor amount of weak paramagnetics. In varieties of mainly ferrimagnetic mineralization polymagnetization decreases in the direction 108 $\rightarrow$ 145.

In the present paper we describe the results of lithologic-paramagnetic investigations of clay-carbonate rocks from the Upper Devonian intersalt complex. Lithologic-magnetic characteristics of these sediments from bore hole Mozyrskaya-1, represented by the Nizhneeletsk subhorizon and the Zadonsk horizon, are given in Fig. 2a.

The Nizhneeletsk section displays marls, carbonate clays, clayey limestone and dolomite, and rare sandstone interlayers. Ferruginous carbonate is frequent and appears as small uneven-

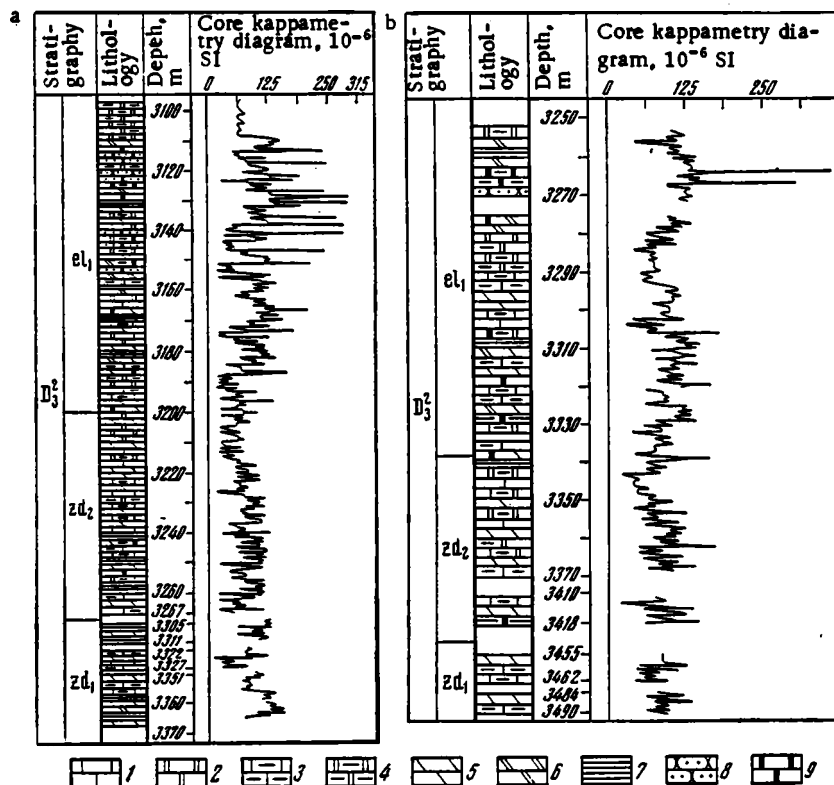


Fig. 2. Lithologic-magnetic characteristics of rocks from the Zadonsk-Elets horizon, bore holes Mozyrskaya-1 (a) and Dudicheskaya-4 (b): 1) limestones; 2) dolomite; 3) clayey limestone; 4) clayey dolomite; 5) calcareous marl; 6) dolomitic marl; 7) clay; 8) sandstone and siltstone; 9) ferruginous carbonate.

ly distributed segregates inclose association with clay material and less often as separate lens of interlayers, mainly confined to the top half of the subhorizon. Except for a homogeneous clay dolomite member at the top ($\kappa = 63-75 \cdot 10^{-6}$ SI), rocks form a finely interstratified bed with extremely diverse kappametric characteristics. Ferruginous carbonate interlayers are distinct on the diagram of the core kappametric study: they are identified by peak maxima ($190-290 \cdot 10^{-6}$ SI). Medium values ($120-170 \cdot 10^{-6}$ SI) are observed in marls and carbonte clays with various ferruginous carbonate concentrations. Marls containing no ferruginous carbonates have a lower suscpetibility: $60-88 \cdot 10^{-6}$ SI. Minimal susceptibility is observed in slightly clayey dolomite and limestone interlayers ($12-37 \cdot 10^{-6}$ SI).

In the Verkhnezadonsk subhorizon, consisting of the same rock varieties, the magnetic susceptibility curve is less differentiated. Ferruginous carbonate does not form interlayers but occurs only as microinclusions dispersed through clay rocks mainly in the middle and lower parts of the subhorizon. Accordingly, these portions exhibit a generally higher susceptibility.

Nizhnezadonsk rocks are of a slightly different composition. Ferruginous-carbonate formations are absent. Susceptibility curve variations are caused by alternations of calcareous clays (maximum level), marls (medium), and clayey limestones with interlayers of "pure" varieties (minimal level).

Table 1 presents the results of a petromagnetic study of rock specimesn of these horizons (bore hole Mozyrskaya-1). The petromagnetic symbols of rocks are correlated with mineralogic characteristics of maximum magnetic fractions obtained by specimen separation. The following notations are used: FC = ferruginous carbonate; D = dolomite; C = calcite; P = pyrite; QF = quartz and feldspar; HB = hydrobiotite; A = anhydrite; OM = organic matter; and F = fragments of volcanogenic rocks. From the data of Table 1 we see that the rocks of the Nizhneel-etsk subhorizon and Zadonsk horizon have different petromagnetic symbols. The main group of ferruginous-carbonate rocks in the Nizhneel-etsk subhorizon is characerized by highly paramagnetic types G and D. It includes parankerites - members of the isomorphous series "magnesium-

TABLE 1

Age	Sam- ple	Composition of maximal fractions of samples, %			Type of magnetic mineralization of rocks							
		κb	G	other minerals	G	D	E		I	K	N,M)	N
el ₁	753	FC -15	15	QF -58; HB -7; P -5	No	No	No	No	No	I-K-d-62	No	No
	754	FC -15	30	QF -38; P -12; HB -5	"	"	"	"	"	I-K-d-59	"	"
	755	D -25	52	P -10; CM10; A-3	"	"	"	"	"	No	"	I-N-i-107
	758	FC -82	15	P -2; A-1	"	"	I-E-b-4	"	"	"	"	No
	762	FC -1	10	QF -85; P -3; HB -1	"	"	No	"	"	"	I-N(M)-n-103	"
	764	FC -15	15	QF -62; HB -5; P -3	"	"	"	"	"	I-K-d-52	No	"
	767	FC -83	15	P -2	IG-6-5	"	"	"	"	No	"	"
	768	FC -84	15	P -1	I-G-6-4	"	"	"	"	"	"	"
	769	FC -79	2	P -1	No	I-D-v-4	"	"	"	"	"	"
	772	FC -78	20	P -1; I- 1	"	I-D-v-4	"	"	"	"	"	"
	773	FC -80	15	P -2; A-3	I-G-B-5	No	"	"	"	"	"	"
	775	FC -87	10	P -3	I-G-g-8	"	"	"	"	"	"	"
	778	—	7	QF -89; P -4	No	"	"	"	"	"	I-N(M)-n-103	"
	779	FC -76	20	P -4	"	I-D-g-8	"	"	"	"	No	"
	783	FC -82	15	P -3	I-G-2-5	No	"	"	"	"	"	"
	787	FC -10	77	QF -5; P -8	No	"	"	"	I-I-b-8	"	"	"
	788	FC -56	31	QF -6; CM4; P -3	"	"	I-Zh-b-33	No	"	"	"	"
	789	FC -8	80	QF -5; P -5; HB -2	"	"	No	"	I-I-a-12	"	"	"
	791	FC -1	15	QF -80; P -4	"	"	"	"	No	"	I-N(M)-i-104	"
	792	FC -80	16	P -2; CM-2	"	I-D-v-5	"	"	"	"	No	"
	795	D-40	52	P -8	"	No	"	"	"	"	"	I-N-zh-107
zd ₂	797	D-50	38	P -7; OM5	"	"	"	"	"	"	"	I-N-zh-107
	798	D-30	52	P -10; CM8	"	"	"	"	"	"	I-N(M)-zh-98	No
	800	FC -25	5	QF -20; P -4; HB 1	"	"	"	"	I-F-b-47	"	No	"
	801	FC -20	72	P -5; HB 2; QF -1	"	"	"	"	I-I-v-8	"	"	"
	802	FC -20	60	QF -17; HB -1; P -2	"	"	"	"	I-I-g-38	"	"	"
zd ₁	804	C -15	75	P -5; CM5	"	"	"	I-Zh-v-9	No	"	"	"
	806	C + D-50	40	P -5; OM5	"	"	"	No	"	I-K-v-10	"	"
	807	C -60	35	P -2; OM3	"	"	"	"	"	I-K-v-9	"	"
	808	C -40	54	P -4; OM2	"	"	"	"	I-I-v-8	No	"	"
	810	C -35	60	P -3; OM2	"	"	"	I-Zh-v-4	No	"	"	"

TABLE 2

Rock age	Sample number	Composition of maximal fractions of samples, %			Type of magnetic mineralization									
		Kb	G	other specimens	G	G	D	E	Zh	I	K	L	N(M)	I
el ₁	402	FC -75	14	P -1	I-V-g-5	No	No	No	No	No	No	No	No	No
	403	FC -80	15	OM2; A-1; P -2	No	I-G-g-5	"	"	"	"	"	"	"	"
	405	FC -75	22	P -3	"	No	"	"	"	I-I-v-11	"	"	"	"
	406	D-95	3	P- 2	"	"	"	"	"	No	"	"	"	I-N-i-107
	441	FC -80	17	P- 1; OM-2	"	"	I-D-g-5	"	"	"	"	"	"	No
	442	C + D -73	20	P -7	"	"	No	"	"	"	"	"	I-N(M)-zh-97	"
	444	FC-60	30	A-5; OM-5	"	"	"	"	I-Zh-g-9	"	"	"	No	"
	445	FC-57	40	P -3	"	"	"	"	I-Zh-g-10	"	"	"	"	"
	446	C-60	35	P -3; F 2	"	"	"	"	No	I-I-d-53	"	"	"	"
	447	C + D -30	50	F 15; P- 5	"	"	"	"	"	No	I-K-a-11	"	"	"
	448	FC + C-55	40	P-3; QF -2	"	"	"	"	"	I-I-g-1	No	"	"	"
	449	C-75	20	QF-3; P -3	"	"	"	"	"	"	"	"	I-N(M)-zh-97	"
	451	FC + C-60	37	P -3	"	"	"	"	I-Zh-g-9	No	"	"	No	"
	452	D-38	60	P -2	"	"	"	"	No	"	"	"	I-N(M)-zh-88	"
zd ₂	460	FC + C-40	55	P -3; HB -2	"	"	"	"	"	I-I-b-11	"	"	No	"
	462	FC + C-45	50	P -5	"	"	"	"	"	I-I-g-9	"	"	"	"
	463	FC + D-45	50	P -3; HB -2	"	"	"	"	"	I-I-v-8	"	"	"	"
	464	FC -40	55	P -3; HB -2	"	"	"	"	I-Zh-g-9	No	"	"	"	"
	469	C + D -75	18	P -7	"	"	"	"	No	"	"	"	I-N(M)-zh-68	"
	470	C-87	7	QF -6	"	"	"	"	"	"	"	"	No	I-N-k-107
	472	FC -35	58	P -6; QF -1	"	"	"	"	I-Zh-g-8	"	"	"	"	No
	475	FC -30	65	P -5	"	"	"	"	I-Zh-v-5	"	"	"	"	"
zd ₁	476	C + D -27	70	P -3	"	"	"	"	No	I-I-b-11	"	"	"	"
	477	C-75	25	—	"	"	"	"	"	No	"	"	I-N(M)-i-102	"
	478	C-68	30 + OM	P -2	"	"	"	"	"	"	"	"	I-N(M)-i-102	"
	479	C-35	58	A-5; OM-2	"	"	"	"	"	"	"	I-L a-8	No	"

dolomite $\text{CaMg}(\text{CO}_3)_2$ - ferrodolomite $\text{CaFe}(\text{CO}_3)_2$," with small amounts (10-20%) of clay matter. They are similar in composition; their refractive indices n_g vary from 1.696 to 1.702. With decreasing parankerite quantity and an increase of clay impurity (specimens 787 and 789) or when parankerite changes for less ferruginous varieties (specimens 758 and 788; n_g of parankerite 1.693 and 1.694, respectively), the paramagnetization of rocks declines to types E, Zh, I, and K. Marl, clayey dolomite, and limestone with no parankerite admixtures belong to types M and N, with the lowest paramagnetization. These types also include samples 762 and 791 from sandy layers, with a small parankerite impurity; sandstones with cement including ferruginous carbonate (~15%) as well as clay (specimens 753, 754, and 764) belong to type K. Highly paramagnetic types G, D, and E are absent in the section of the Verkhnezadonsk horizon. The highest paramagnetization is exhibited by specimens of carbonate-clay rocks (800-802) from the lower portion of the subhorizon. These belong to types I and K, i.e., have the same paramagnetization as specimens 787 and 789 of the Nizhneeletsk subhorizon, although they contain twice as much ferruginous carbonate. The difference is due to a lower ferruginosity of the latter (ferruginous dolomite, refractive indices 1.684-1.688). The lowest paramagnetization levels, N and N(M), are observed in marl specimens from the subhorizon roof.

Petromagnetic investigation of ferruginous carbonate from Nizhneeletsk and Verkhnezadonsk subhorizons yielded data consistent with the results of chemical analysis. Petromagnetic characteristics reflect the ferruginosity of parankerites, as confirmed by a comparison of paramagnetic specimen types and FeO content in them (%):

Type G (spec. 768) — 6.86	Type E (spec. 758) — 4.72
" (spec. 773) — 6.84	Type Zh (spec. 788) — 4.30
Type D (spec. 779) — 5.36	Type I (spec. 800) — 2.30
" (spec. 792) — 5.09	" (spec. 802) — 2.0

Marl and calcareous clay specimens from the Nizhnezadonsk subhorizon contain no ferruginous carbonate. Their paramagnetization (types Zh, I, and K) is determined by the heightened paramagnetization of clay minerals.

Intersalt sediments from Dudichskaya-4 borehole (Fig. 2b) consist of the same lithologic varieties as rocks from Mozyrskaya-1. Unlike the latter, the section of Nizhneeletsk subhorizon in this hole contains no numerous ferruginous carbonate interlayers; the rare interlayers that do occur have a high paramagnetization level (peak susceptibility of $315-365 \cdot 10^{-6}$ SI); the Nizhneeletsk sediments are more clayey and contain almost no sand interlayers. The subhorizon consists mainly of parankeritic marl and clay ($\chi = 100-175 \cdot 10^{-6}$ SI) with interlayers of clayey dolomite and limestone ($\chi = 35-63 \cdot 10^{-6}$ SI).

In the Verkhnezadonsk part of the section, the average level of the curve is slightly lower, but in areas of parankeritic marl with largest parankerite content susceptibility rises to $125-150 \cdot 10^{-6}$ SI.

Highly paramagnetic carbonate formations of the Nizhneeletsk subhorizon (Dudichskaya-4 borehole) are distributed between types V, G, and D (Table 2). Specimens of type V, not found in Mozyrskaya-1 cores, are weakly clayey ankerite varieties (refractive indices of 1.704-1.706), which, according to a chemical analysis, contain 9% FeO. The main group of ferruginous-carbonate rocks in the Nizhneeletsk and Verkhnezadonsk subhorizons belong to types Zh and I; it consists of parankeritic marl and clay and rarely clayey parankerites of a slightly ferruginous variety (specimen 405). Some marls from the lower portion of the Nizhneeletsk and the upper portion of the Verkhnezadonsk subhorizons include an association of ferruginous carbonate with a microgranular calcite; the latter is probably epigenetic, developed after ferruginous carbonate. Proportions of the two carbonates have not been determined, but since all specimens, with rare exceptions, belong to type I, they are of an identical composition. Marls with no ferruginous carbonate have weak and medium paramagnetization. They include varieties with small fragments of effusive rocks (specimens 446 and 447). Their grades (I) exhibit no obvious signs of ferritic mineralization; the fragments consist mainly of plagioclase laths and are intensely carbonatized. Traces of ferrite relicts have been preserved, as indicated by species a and d. Interlayers of clay limestones and dolomites in the sections of the Nizhneeletsk and Verkhnezadonsk subhorizons belong mainly to low-mineralization types: N and N(M).

Specimens of marls and calcareous clays in the Nizhneeletsk subhorizon with the paramagnetization controlled by the amount of clay admixture are divided between types I, L, and N(M).

TABLE 3

Hole (number of specimens)	Age	Petromagnetic rock type	X-ray structural analysis data, %			
			M	H	C	K
Mozyrskaya-1 (4)	Elets horizon	I, K, M, N	60—70		0—5	25—40
Mozyrskaya-2 (4)						
Prudokskaya-1 (3)	Same	L, M	40	35—40		20—30
Mozyrskaya-1,2 (3)	Verkhnezadonsk subhorizon	Zh, M, N	60—75	—	0—5	25—35
Mozyrskaya-1,2	Nizhnezadonsk subhorizon	Zh, I	70—80	—	—	20—30
Davydovskaya-20 (2)	Alatyr horizon	D, E	75—80	—	0—5	15—20
Malodushinskaya-19 (2)	Same	D	100	—	—	—
Mozyrskaya-1 (4)	Kynov horizon	D, E	90—100	—	—	0—10
Dudichskaya-4	Same	D, E	100	—	—	—
Davydovskaya-18 (6)	»	D, E	90—100	—	—	0—10
Northern Kalinovskaya-1 (7)	»	G, D, E	100	—	—	—
Marmovicheskaya-2 (2)	»	E	100	—	—	—

Note. M = mixed-layer hydromica-montmorillonite phase; H = hydro-mica; C = chlorite; K = kaolinite.

A brief description of additional symbols in the notation of these rocks from Mozyrskaya-1 and Dudichskaya-4 is given below. In all the horizons all rock varieties belong to degree I and have no obvious signs of ferrimagnetic mineralization ($CM_{0.2} < 0.01$). Most specimens display species characteristics typical for paramagnetic mineralization with a predominance of highly paramagnetic species b, c, and d; these are frequent in ferruginous-carbonate formations of the Nizhneeletsk and Verkhnezadonsk subhorizons. Marls and carbonate clays of the Nizhneeletsk subhorizon, clayey dolomite and limestone, and marl from the Verkhnezadonsk and Nizhneeletsk subhorizons belong to the medium paramagnetization species zh, i, and k. Sandstones of the Nizhneeletsk subhorizon and some of the varieties of carbonate clays and marls from Nizhneeletsk and Nizhnezadonsk subhorizons belong to latent ferrimagnetization species a, d, and n, indicating an admixture of finely dispersed pyroclastics or particles of decayed volcanogenic rocks with ferrite relicts. The latter are too fine to be separated as a fraction $CM_{0.2}$; mostly, they cannot be discerned under a microscope. Traces of ferrite in specimens of this group are confirmed by high values of their coefficient E (in particular, specimens 753-200; 754-148; 764-158; 446-100; 447-100).

By varieties, most specimens belong to the first antiferro-paramagnetic group (1-66), i.e., are characterized by a large yield of maximal paramagnetic fraction ($\Pi_{M_{max}}$), a small value of the parameters I_{ts} that characterizes the homogeneity of the fraction, and a low value of the nonmagnetic fraction (Π_H). Specimens of ferruginous-carbonate rocks have the lowest variety values; sandstones have the highest values. Clay-carbonate rocks of types N and N(M) consist of calcite, dolomite, and clay mineral admixture; they include varieties of the second weakly paramagnetic-diamagnetic group that differs from the former by larger parameters I_{ts} and Π_H and a much smaller amount of the paramagnetic fraction ($\Pi_{M_{pr}}$). Clay material is contained in this section in subordinate amounts; wherever more clay is present it consists of weakly ferruginous varieties.

Besides paramagnetic studies of carbonate and clay-carbonate sediments, a similar study has been conducted of clay rocks from intersalt and some of the horizons of the subsalt Devonian complex. In order to determine the correlations between petromagnetic characteristics of these horizons and their composition, x-ray structural analyses have been performed of clay material from intersalt and subsalt rocks in several bore holes of the Pripyat trough. The

results of the comparison of generalized typical characteristics of clay rocks and the data of their x-ray diffractoscopy are given in Table 3. There is a consistent difference in petromagnetic and x-ray structural characteristics of clay rocks. Clays from the Elets horizon exhibit a broader range of types I, K, L, M, and N, with a predominance of weakly paramagnetic varieties. Clays from the Zadonsk horizon belong to weak and medium types of paramagnetization: Zh, M, and N (zd_2) and medium paramagnetization Zh and I (zd_1). Accordingly, the quantity of S (and G) is increased and the amount of kaolinite phase is decreased. The reduction of clay paramagnetization could involve not only an increased proportion of kaolinite component, but a lowering of the ferruginosity of mixed-layer minerals. The paramagnetization of clays and clay-carbonate rocks can be gauged by the quantitative ratios of their carbonate and clay components. In particular, in the Nizhneeletsk subhorizon in holes Mozyrskaya-1 and Dudichskaya-4 dolomitic marl, despite the high (>50%) clay content, belongs to the types N(M) and N, meaning that the clays are weakly paramagnetic. Similar specimens have also been found in the upper portion of the Verkhnezadonsk horizon in the Mozyrskaya-1 section. In the parankeritic marls of the lower half of zd_2 in this hole clay paramagnetization is much higher, because, despite small amounts of parankerite and its low ferruginosity, the rocks belong to type I. Clayey rocks of the subsalt complex have a higher paramagnetization and a greater homogeneity of paramagnetic types: D, E and rarely G. X-ray structural characteristics are also uniform: the phase S 90-100%; kaolinite admixture is either absent or present in minor amounts.

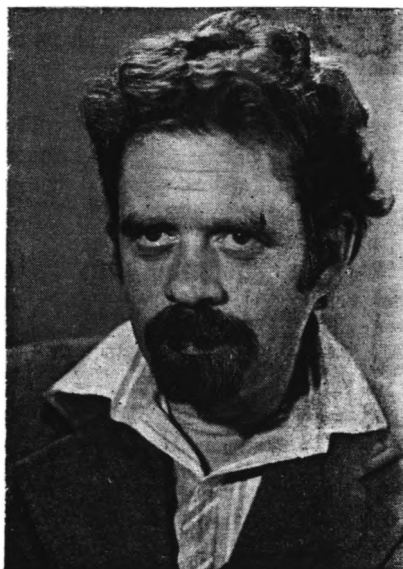
The greater diversity of clay rock characteristics in the intersalt bed as compared with the subsalt state suggests that more intense and varied geochemical processes evolved in the former. The low paramagnetization of clays in the Nizhneeletsk subhorizon and their close association with ferruginous carbonates indicate that during diagenesis ankeritization of dolomites was accompanied by kaolinization of clays. Similar processes also evolved in the Verkhnezadonsk subhorizon, although at a lower rate.

The lithologic-petromagnetic study of clay-carbonate and clayey rocks has shown a distinct differentiation of magnetic mineralization types. Lithologic-petromagnetic characteristics can be used to determine ferruginous-carbonate formations in sections and to compare them for multifaceted analysis of the geochemical settings of sediment formation, diagnosis and classification of clay minerals, evaluation of clay content in carbonate rocks (including carbonate collectors), separation and correlation of bore hole sections, isolation of portions in sedimentary rocks with an admixture of finely dispersed volcanogenic material, and evaluation of the occurrence boundaries of that material.

LITERATURE CITED

1. F. N. Efimov, Kappametric and Magnetic-Fractional-Mineralogic Investigations of Sedimentary Formations [in Russian], Nedra, Moscow (1969).
2. F. N. Efimov, "A classification system for petromagnetic information," Sov. Geol., No. 7, 31-53 (1978).

VIKTOR ZAKHAROVICH BLISKOVSKII



On September 16, 1987, V. Z. Bliskovskii, Doctor of Geological and Mineralogical Sciences, chairman of the laboratory of technological mineralogy of the Department of Geology of the State Scientific-Research Institute of Mineral and Chemical Raw Materials, died after a serious illness. Geological science and the Mining-Chemical Industry has lost a prominent scientist in the field of lithology and mineralogy, a major researcher of phosphorites, and a fine human being.

Viktor Zakharovich was born on February 7, 1936 in Moscow, the son of a journalist. After graduating from the Geological Exploration Faculty of the I. M. Gubkin Institute of Petroleum, Moscow, in 1958 he was assigned for 3 years to work at the Yakutsk Geological Administration.

In 1961 Viktor Zakharovich returned to Moscow and started working at the Geological Laboratory of the State Scientific-Research Institute of Mineral and Chemical Raw Materials, where he researched the geochemistry of phosphorites. From 1967, during the next 5 years, he headed the Department of Scientific and Technical Information and continued his study of geochemistry of impurities in phosphorites. In 1969 V. Z. Bliskovskii defended his candidate's dissertation at the Institute of Mineralogy, Geochemistry, and the Crystallochemistry of Rare Earth Elements (Soviet Academy of Sciences), in which he stated a range of the interesting characteristics of the geochemistry of impurities in phosphorites.

In 1972 V. Z. Bliskovskii led the way in developing technical mineralogy. His scientific capability and hard work were recognized and he was generally acknowledged as a scientific leader in the field of the research of phosphate ore.

Based on his complex research in the material composition of phosphorites and its influence on their nature, Bliskovskii defended his doctoral dissertation at the All-Union Scientific-Research Institute of Mineral Raw Materials in 1983. That same year, his outstanding monograph on this topic was published. He demonstrated the basic mineralogical and petrographic factors determining the technological characteristics of different phosphorites and their enrichment.

With great efforts V. Z. Bliskovskii organized the All-Union Conference for technological mineralogy of phosphorite ore, but died suddenly. That conference took place and was dedicated to his memory.

V. Z. Bliskovskii was among the foremost geologists-phosphatists and was widely known in the Soviet Union as well as abroad. He authored over 120 scientific articles and monographs.

Translated from *Litologiya i Poleznye Iskopaemye*, No. 4, pp. 141-142, July-August, 1988.

V. Z. Bliskovskii was a man of high moral standards. He was modest, had a high capacity for work, and placed high demands on himself; these traits won him great respect and authority. A member of the Communist Party of the Soviet Union since 1971, V. Z. Bliskovskii was very active in public work; he was a member of the Interdepartmental Lithologic Council of the Academy of Sciences of the USSR, a member of the Commission on Technological Mineralogy of the All-Union Mineralogical Society, and a member of the Scientific Council on Defending Dissertations at the Sergo Ordzhonikidze Institute of Geological Exploration, Moscow.

During his short life Viktor Zakharovich accomplished much. His bright memory will forever remain in the hearts of his friends and associates.

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